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ADVISORY GROUP FOR AEROSPACE RESEARCH & DEVELOPMENT

Stress Corrosion Cracking in Aircraft Structural Materials

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NORTH ATLANTIC TREATY ORGANIZATION



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NORTH ATLANTIC TREATY ORGANIZATION
ADVISORY GROUP FOR AEROSPACE RESEARCH AND DEVELOPMENT
(ORGANISATION DU TRAITE DE L'ATLANTIQUE NORD)

STRESS CORROSION CRACKING
IN AIRCRAFT STRUCTURAL MATERIALS

Report of a two-day Symposium held by the Structures and Materials Panel of AGARD,
in Turin, Italy on 18 and 19 April 1967

FOREWORD

Arising from its successful one-day symposium on corrosion of aircraft, held in April, 1966 and described in AGARD Report 540, the Structures and Materials Panel of AGARD held a two-day symposium on stress corrosion cracking in April 1967 in Turin, Italy. Mr H.G.Cole, Ministry of Technology (Aviation Group) UK, was retained to plan and monitor the meeting, to edit the papers and to report the discussion.

The symposium was attended by over a hundred delegates from the NATO nations, drawn from aircraft constructors, metal manufacturers, independent research organisations, Universities and Government departments (including Serving Officers). Seven formal papers covering general theory, aluminium alloys, nonstainless steels, stainless steels and titanium alloys were followed by seven national surveys that described the current research and development work on stress corrosion cracking.

The large attendance, the high level of the papers, and the liveliness of the discussion all testified to the importance of the stress corrosion cracking phenomenon and the Panel acknowledges with thanks the parts played by Mr Cole, the authors, the contributors to the discussion and the attendees in ensuring the success of the symposium.



Noel H. Mason
Chairman, Structures and Materials Panel

AVANT-PROPOS

Comme suite au symposium de un jour sur la corrosion des avions tenu en avril 1966 et décrit dans le Rapport No. 540 de l'AGARD, la Commission "Structures et Matériaux" de l'AGARD a organisé pour avril 1967 à Turin, Italie, un colloque consacré à l'étude de la fissuration due à la corrosion sous tension. Mr H.G.Cole du ministère de la Technologie (Groupe Aviation) du Royaume-Uni a été nommé pour établir le programme, contrôler la réunion, préparer les textes pour la publication et rendre compte des discussions qui ont suivi les exposés.

Ont participé au symposium plus de cent délégués des pays OTAN, parmi lesquels se trouvaient des représentants des constructeurs d'avions, industries métallurgiques, organismes de recherche autonomes, universités, services gouvernementaux (y compris les Forces Armées). Sept exposés couvrant les principes, les alliages d'aluminium, les aciers non inoxydables, les aciers inoxydables, et les alliages de titane ont été présentés suivis de sept mémoires donnant un aperçu des travaux de recherche et de développement effectués sur le plan national sur la fissuration par corrosion sous tension.

L'assistance nombreuse, le niveau élevé des exposés et la vivacité des discussions ont témoigné de l'importance du phénomène des fissures dues à la corrosion sous tension et la Commission tient à remercier Mr Cole, les auteurs, tous ceux qui ont participé aux discussions et enfin tous les congressistes pour leurs contributions respectives au succès du symposium.

N. H. Mason
Le Président de la
Commission "Structures et Matériaux"

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EDITOR'S NOTE

In the reports of the discussions that followed the papers, all premature failure due to the conjoint action of tensile stress and corrosion is called Stress Corrosion Cracking, (SCC) whether the mechanism is by Active Path Corrosion, Hydrogen Embrittlement, or by any other mechanism.

The reports have not been checked with the speakers, and are the sole responsibility of the Editor.

H. G. Cole

GENERAL THEORY OF STRESS CORROSION

by

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GENERAL THEORY OF STRESS CORROSION

Mars G. Fontana

Stress corrosion is the degradation of materials by the conjoint action of tensile stress and corrosion. For the purposes of this paper, stress corrosion is considered to be the premature environmental cracking of alloys. In practically all cases of stress corrosion, common features are (a) brittle fracture or essentially no gross ductility, (b) corrosion is localized with little if any general overall attack, (c) failure is premature based on strictly mechanical considerations, and (d) specificity of the alloy-environment system.

The devastating effects of stress corrosion can be illustrated by comparing it to a stress-temperature system and also by short cracking times. Type 304 stainless steel fails in boiling magnesium chloride at approximately the same time and stress as stress-rupture at about 1300°F. This same steel will crack in a few hours at a few thousand lb/in.² under chloride concentrating conditions at 100°F. Brasses and ultra-high strength steels can be made to crack in seconds and minutes. As we move in the direction of higher strength alloys to improve cost and performance considerations in aerospace and industrial plant applications, knowledge of mechanisms and effective mitigation of stress corrosion are necessary. The ultimate goal is quantitative predictive capabilities and reliable design data. In fact, stress corrosion is one of our most important corrosion problems and millions of dollars are being spent annually in many laboratories on studies of this problem. This is a challenge that must be met.

Many mechanisms of stress corrosion for numerous alloy-environment systems have been proposed. In all cases they apply directly only to the system involved. In many cases, they are really not 'mechanisms' but a description of conditions, steps, or processes operating for the given system. The specificity of stress corrosion - examples are titanium alloys - N_2O_4 , austenitic stainless steel - chloride waters, and brass-ammonia - indicates that a single, general, unified mechanism for all systems is not likely. The interplay between alloy, interface, and environment is indeed complex. As an aside and further to complicate the problem, nonmetallics also exhibit environmental cracking. For example as-cast epoxy resins crack in certain caustics, acids, and solvents; stress relief heat treatments stop cracking, and applied stress causes cracking - they behave in a manner similar to alloys!

Cracking failures have been described as stress corrosion, stress-corrosion cracking, corrosion cracking, season cracking, caustic embrittlement, sulfide-stress cracking, hydrogen embrittlement, and hydrogen-stress cracking. All of these are more or less related although some distinction can be made between stress corrosion and hydrogen embrittlement. Figure 1 illustrates schematic differentiation between the two modes of cracking¹. Stress corrosion involves dissolution of metal at the advancing tip of the crack. If anodic currents promote cracking, the system is anodically sensitive

and the cracking is stress corrosion. Hydrogen embrittlement involves brittle fracture assisted or catalyzed by hydrogen. If cathodic currents promote cracking, the system is cathodically sensitive, and cracking is due to hydrogen embrittlement. Austenitic stainless steels are a good example of anodically sensitive alloys. High strength steels are susceptible to hydrogen embrittlement. However, this is not to say that these modes of cracking are always separate and distinct. In many cases they operate simultaneously.

Conditions for stress corrosion can be summarized as follows:

$$(\text{alloy susceptibility})^n \times (\text{environmental aggressiveness})^m \times (\text{stress intensity})^p \geq \text{constant of the system.}$$

If one of these factors is zero, cracking will not occur. If one factor is relatively low then another factor could be relatively higher for cracking to occur in a given time.

Crack morphology varies from almost straight lines to branching and "river delta" patterns. Figure 2 illustrates intergranular, transgranular, and transgranular cracks with branching. These are properly labelled cracks even though they might progress because of local dissolution at the tip. Sometimes both intergranular and transgranular cracks are observed together. In magnesium alloys, the mode of cracking can be changed from one to the other by heat treatment or changes in the environment, so one alloy does not always have its own specific crack morphology. Many years ago a transgranular crack was erroneously interpreted as corrosion fatigue and an intergranular crack as stress corrosion. The appearance of the surface of the fracture (fractographs) is essentially identical in most cases for both stress corrosion and hydrogen embrittlement for a given alloy. Cracks always progress normal to the direction of the stress except in rare cases when a crack is observed as far off as ninety degrees from the direction of applied stress.

Strengthening mechanisms for metals and alloys include (a) precipitation of a second phase from solid solution (aging), (b) martensitic hardening, (c) strain hardening (cold work), (d) duplex structures (austenite and ferrite in stainless steels), and (e) solid solution hardening. All except the latter tend to destroy the homogeneity of the alloy and/or involve residual stresses which could contribute to the localized attack and stress levels generally required for stress corrosion.

Metallurgical factors are important in stress corrosion. These include preferential orientation of grains and grain size, composition and distribution of precipitates, dislocation interactions, progress of phase transformations, and others discussed below. It is difficult to evaluate the effect of changes in microstructure in themselves on the resistance of high strength steels to stress corrosion because changes in microstructure in a large measure change the strength of the steel. The stress corrosion resistance of quenched Types 403 and 410 martensitic stainless steel does not change appreciably with tempering temperature until about 1100°F when the resistance to stress corrosion increases tremendously. However, the hardness and strength decrease. Additional studies on this alloy in our laboratory showed the drastic effect of manganese sulfide inclusions. Cracks started within 30 seconds at the base of the pit formed by dissolution of the inclusion.

Grain size can have an important effect on susceptibility to stress corrosion but this can often be associated with second phases. Some claim grain shape is more

responsible in aluminum alloys than any other metallurgical factors. For maraging steels, small grains show much better resistance to stress corrosion than large grains. Parkins² has shown that grain boundary carbides in mild steels are cathodic to the surrounding ferrite. Tiner and Gilpin³ observed a similar phenomenon in 4340 steel where the carbide remained unattacked and the surrounding ferrite was dissolved. Cracking of low and high alloy steels follows prior austenite grain boundaries probably because of compositional differences in these (anodic) areas.

High strength aluminum alloys exhibit susceptible intergranular crack paths. They also show greater susceptibility in the direction transverse to forging or rolling direction.

Some publications in the literature claim immunity for tangled dislocation structures and susceptibility for coplanar dislocation arrays. We believe that there is no unique correlation between dislocation coplanarity as viewed in thin foils and susceptibility to cracking.

Composition is important because it can markedly affect the resistance of alloys to uniform corrosion and localized attack. Figure 3 shows stress corrosion of stainless steel wires in magnesium chloride as a function of nickel content (added to 18 Cr-Fe base)⁴. Kirk et al.⁵ showed essentially the same cracking behaviour for Types 347 and 316 in chloride waters at 400°F. Carbon improves resistance and nitrogen, phosphorus, and some other elements have deleterious effects on the austenitic stainless steels.

Figure 4 shows the effect of carbon content on cracking time of mild steel in a nitrate solution². In sulfide solutions and for a given strength level, low alloy, quenched and tempered steels are less susceptible to cracking than more highly alloyed steels⁶. Additions of molybdenum, manganese, and nickel are reported to increase susceptibility and chromium decreases it in sulfide solutions. Maraging steels are less sensitive to hydrogen embrittlement than the more conventional martensitic steels.

Minor elements affect the susceptibility of high strength aluminium alloys to stress corrosion.

In some systems such as Fe-Cr-Ni and Cu-Au, surface enrichment of the more noble component can occur with attendant effects on stress corrosion.

In the past it has been a common generalization that pure metals do not crack. However, Pugh⁷ observed cracking in 99.999% copper in the presence of $\text{Cu}(\text{NH}_3)_5^{+2}$ complex ions.

Compositional variables also affect the entry and also diffusion of hydrogen in carbon steels. Hydrogen embrittlement is not a factor in copper alloys and aluminum alloys.

Environments are usually specific with regard to stress corrosion of alloys. 18-8 stainless steel is very susceptible to chloride-waters but annealed carbon steel is not susceptible in this environment. Exclusion of oxygen stops cracking in the former combination.

Under chloride concentrating conditions 18-8 cracks in a few hours at applied stresses of a few thousand lb/in.² (Ref. 8). Wetting and drying conditions in chloride environments are aggressive to carbon steels and stainless steels, particularly the latter, because of concentration of chlorides. Distilled water in some cases cracks high strength steels faster than 3% NaCl. Mattson⁹ showed very rapid cracking of brass in ammonia solutions in a narrow pH range around 7.3 and relates this phenomenon to the presence of a tarnish film. Pugh⁷ demonstrated the specificity of the complex ion $\text{Cu}(\text{NH}_3)_5^{+2}$ for cracking of brass. Brasses do not crack in chloride waters.

Cracking of titanium alloys in non-aqueous liquids for example Ti6Al4V by nitrogen tetroxide or methanol, can be inhibited by addition of small amounts of water presumably because the water forms a passive film.

Leckie¹⁰ showed that for a given stress-intensity ratio in 3% sodium chloride, susceptibility or immunity to stress corrosion was dependent on the method of loading pre-cracked specimens of alloy Ti-7Al2Cr1Ta. When the load was applied in air and then the chloride solution added, the specimen did not crack. When the same load was applied to the specimen immersed in the solution, the specimen failed within a few minutes. Apparently loading of the specimen in the solution cracks the protective film and rapid initiation and propagation of the cracks occurs. Preloading in air permits the oxide film to heal itself. Leckie believes the behaviour of the oxide film is most important in titanium alloys with alloy composition and heat treatment of minor importance.

Adsorption of some constituent of the environment on the metal could change the surface energy situation and thereby result in easy tearing or corrosion of this "weakened" surface.

The question of environmental specificity may eventually be found to apply less in the case of cracking of the high strength alloys. Many of these alloys, notably the high strength steels and certain high strength titanium alloys appear to crack by essentially a hydrogen embrittlement process. In these cases, cracking will be favoured by any environment-metal system which promotes the entry of hydrogen into the metal. Such systems would tend to promote:

1. Weakening of protective film
2. Enhancement of the cathodic reaction
3. Increased coverage of hydrogen on the surface of the metal
4. Higher solubility of hydrogen in the metal
5. Higher diffusivity of hydrogen in the metal.

Alloys and environments which reverse these trends would tend to reduce the cracking tendency.

The important point to emphasize here is that not all environments cause cracking and not all alloys are susceptible to cracking in a given environment.

Tensile stresses of sufficient magnitude to cause cracking are often present. They may be stresses due to welding, thermal gradients, applied loads, or residual stresses due to heat treatment, coldworking, cutting, and grinding. Local microstructural stresses are almost impossible to calculate. There may be threshold values of stress for a given alloy environment combination but these must be used with caution. Applied stresses are not of the greatest consequence in earth bound structures, but "safety"

factors in design are more critical for hydrospace and aerospace applications. In many cases, a crack starts at the base of a pit⁵. These pits act as notches and stress raisers. Saucer-shaped pits usually are not effective in this regard. Parenthetically, the process responsible for a pit will also produce hydrogen which could increase the local embrittlement. Another source of stress is the wedging action of solid corrosion products within the crack. Pickering¹¹ observed wedging stresses in 18-8 near its yield point and demonstrated crack propagation because of this stress. This situation would not apply where the corrosion products are soluble.

Applied stress and prior crack length are related in high strength steels. This effect is combined in fracture mechanics analysis which leads to the concept of the stress intensity factor K . No cracking will occur in an inert environment until the stress intensity factor exceeds a certain minimum value. When this value is exceeded the crack proceeds at a catastrophic rate (fast fracture). This critical stress intensity is termed K_{IC} . On the other hand cracking will start in a suitable environment at an initial K_I which is below K_{IC} . When the crack reaches a sufficient depth and K_I reaches K_{IC} , the crack proceeds catastrophically. As K_I is lowered progressively below K_{IC} , the crack stops. The value of K_I below which cracks stop or do not progress in a cracking environment is termed K_{ISCC} . Development of high strength steels with higher values of K_{IC} and, of course, higher values of K_{ISCC} , should be helpful. Figure 5 from Brown and Beachem¹² shows the relationship between K_{II} (initial value of stress intensity) and time to fracture (TTF) for 4340 steel. Below a value of about 53 cracking does not occur. Figure 6 from this same work with slight modification shows that fast fracture will not begin until K_{IC} for non-environmental cracking is reached.

Priest et al. were perhaps the first to utilize cracked specimens to study the propagation of stress corrosion. Notches and machined slots proved unsuitable so the specimen was cracked and then the tip observed as the crack progressed. Steigerwald¹⁴ studied stress corrosion of specimens precracked by fatigue and also Brown¹⁵. The latter used large specimens to obtain conditions of plane strain wherein the zone of plastic deformation is contained in a zone of elastic deformation. Steigerwald used thinner specimens.

Cold worked austenitic stainless steels resist greater stresses and longer TTF as compared to annealed material.

Strength level of high strength steels is the most important parameter for susceptibility to stress corrosion. Phelps¹⁶ states that in chloride environments most steels with yield strengths below 180,000 lb/in.² are resistant. Between 180,000 lb/in.² and 210,000 lb/in.², resistance may be obtained depending on the specific steel and heat treatment. At yield strengths over 210,000 lb/in.² steels hardened by heat treatment are generally susceptible to stress corrosion. In sulfide-containing or similar environments yield strengths of about 115,000 lb/in.² and higher are generally susceptible.

Hydrogen can enter metals and alloys in many ways. These include corrosion in service, pickling, cathodic protection, electroplating, cathodic charging, and dissociation at high temperatures. "Poisons" such as sulfur and selenium hasten the process. Only "atomic" hydrogen can enter and diffuse--molecular hydrogen does not. The atomic hydrogen must enter and diffuse to the crack tip area as shown in Figure 1.

Entrance and diffusion are affected by surface films, and alloy composition. Aluminum and copper are not subject to hydrogen embrittlement. A good example of an unusual case is embrittlement of tantalum when it is in contact with a corroding metal. In this case the process is irreversible from the practical standpoint. Figure 7 shows the strong effect of hydrogen on fatigue strength of 4340 and also the difficulty in completely removing cathodically charged hydrogen²⁹.

Boyd and his associates¹⁶ at Battelle-Columbus postulate the formation of susceptible crack paths in 13-8 stainless steels because of the formation of hydrides or hydrogen enriched phases.

Initiation and propagation are the two important steps in stress corrosion. In the so-called passive metals a fault in the passive film is often an initiation site as demonstrated by Leckie¹⁰ for titanium and many others for stainless steels and aluminum alloys. Staehle¹⁵ shows schematically in Figure 8 the damage to a protective film by an active slip step. Localized corrosion occurs at the emerging slip step. Continuous emergence of slip steps is a dynamic process and could explain why severely deformed metals (before exposure to a corrosive) do not exhibit sufficiently high corrosion rates to account for rapid penetration of cracks. Many have proposed active sites due to emerging dislocations and other dislocation-structure interactions. In most cases, a sharp pit forms and the crack initiates at the bottom of the pit.

Haynie and Boyd²⁷ propose the following for the mechanism of the initiation of stress corrosion in aluminum alloys:

"Strain-induced absorption of hydrogen at mechanically weak grain boundary zones reduces the energy of activation for the corrosion of these zones. The hydrogen is produced at local cathodes and diffuses through the grains to the grain boundaries. The slow rate of diffusion accounts for the "incubation period" associated with the initiation of stress-corrosion cracks. This mechanism also explains why materials susceptible to stress-corrosion cracking are not necessarily susceptible to intergranular corrosion."

The role of tensile stress in rupturing films on brass has been described by Forty²⁰. The film forms and ruptures, the film re-forms at the base of the crack and again ruptures -- the process is repeated until failure of the specimen occurs. Examination of the fracture surface shows steps and striations.

Staehle¹⁹ and others have proposed the formation of surface layers enriched in the more noble component of the alloy because of corrosion. A fault in this layer exposes active substrate metal and rapid localized anodic attack results.

In the case of intergranular cracking, the grain boundary regions could be more anodic, or less corrosion resistant because of precipitated phases, depletion, enrichment, or absorption, thus providing a susceptible path or a "weakened" metal path. Chloride ion could be adsorbed in the intergranular "trenches" of sensitized 18-8 steels during fabrication, pickling, and cleaning procedures. These sites then initiate cracking when the equipment is later subjected to essentially chloride free water and high temperatures during actual operation.

Figure 9 shows a panoramic view of possible critical processes which may influence environmentally accelerated fracture¹.

Nielsen's²¹ excellent electron metallography shows tunnels that form in 18-8 steels. These may be initiating sites for cracks. Recent work by Dean and Staehle²² shows that these tunnels occur in several stainless steel compositions.

Bhatt and Phelps²² report on an extensive study of the effect of electrochemical polarization on the stress corrosion behaviour of steels with high yield strength. In many instances these experiments demonstrate whether or not cracking is caused by an active path or by hydrogen embrittlement. Potential and pH ranges over which each mechanism is operative are delineated.

The *conjoint* action of stress and corrosion required for crack propagation in a magnesium alloy was demonstrated by Priest¹³. The advancing crack was stopped when impressed current cathodic protection was applied and started again when the current was removed. The cycle is repetitive until catastrophic fracture occurs. The repetitive starting and stopping of the crack was filmed (movie) and projected at actual speed of propagation.

Some investigators claim that stress only increases dissolution because of greater anodicity at the tip of the crack as shown in Figure 1. This may be due either to the increase in local strain energy or to the rapid emergence of slip steps. The contribution of the strain energy *per se* is a doubtful factor because even at high stresses there is a negligible effect on the electrode potential. The role of rapid slip step emergence is probably the significant consideration. Such rapid emergence does not make the crack *more* anodic but rather *continuously* anodic. In this case the crack would be an "elongated pit". Pardue²⁴, using audioamplification showed that a periodic mechanical step or jump occurred during crack propagation. In fact, "pings" were heard with the naked ear.

After a crack is initiated, local conditions become quite favourable for propagation. Strain is released in the crack walls but intensity is increased at the apex of the crack. In addition, the walls may become cathodic to the anodic tip. Changes in pH in the crack could also alter the corrosion picture.

"THEORIES", "MECHANISMS", "OPERATING STEPS"

In view of the foregoing and other considerations, the following are presented for consideration as possibilities (not in any particular order of preference or chronology):

1. Stress corrosion and hydrogen embrittlement are two separate and distinct mechanisms.
2. Same as 1 except they are intimately related.
3. Cracks propagate by alternate stages of pitting and mechanical tearing.
4. Cracks propagate only because of dissolution at the base of the crack.
5. Stress at the base of the notch ruptures a passive film or layer and the exposed metal then dissolves at a rapid rate. If the tip repassivates, the process repeats itself.
6. Metal at the base of a crack becomes more anodic as a consequence of plastic deformation.

7. Hydrogen is absorbed during progress of local cathodic reactions. Hydrogen diffuses to the stressed region at the tip of the crack. This region is both anodic and brittle. The crack progresses by a combination of anodic dissolution and mechanical fracture.
8. Hydrogen plays a role in *all* stress corrosion failures.
9. Tunneling results in stresses sufficiently high to initiate fracture.
10. Metal is embrittled by oxidation or selective leaching. Cracks form in the embrittled region and propagate short distances until they are stopped by plastic dissipation in the ductile region. The embrittlement reaction again operates and the process repeats itself.
11. Cracks propagate because of the high stresses induced by the wedging action of corrosion products.
12. Corrosion only plays a role in the initiation of cracks. Propagation is strictly mechanical.
13. In cracking systems, the critical chemical reactions depend on the local potentials at the electrode surfaces. Unless the metal-environment chemistry is of a proper combination, these potentials cannot be achieved and the required reactions will not occur.
14. Adsorption weakens the metal by lowering the surface energy and it is easily torn or more readily corroded.
15. An enriched surface layer is anodic to the substrate and localized attack occurs on the latter when a fault exists in the more noble layer.
16. The integrity and chemistry of the oxide or surface film determines primarily whether or not stress corrosion will occur.
17. Absorbed chlorides are primarily responsible for stress corrosion.
18. A susceptible crack path must exist or stress corrosion will not occur.
19. Stress corrosion only occurs at temperatures above room temperature.
20. Diffusion of hydrogen is the rate-controlling step in stress corrosion.
21. If the hydrogen results from a corrosion reaction, the phenomenon is stress corrosion. If hydrogen comes from another source, i.e. electroplating, it is hydrogen embrittlement.

Elucidation of these points will doubtless be made by subsequent speakers including pros and cons.

No attempt has been made in this paper to present a complete bibliography. You are referred to Hugh Logen's recent book²⁵ for this aspect.

The names of many workers in the field of stress corrosion have been omitted because of lack of time and space. References 26 and 27 are very informative for high strength steels and aluminum alloys. The Corrosion Information Center²³ at The Ohio State University has most of the significant publications on stress corrosion on file.

An acceptable theory or mechanism should explain all of the experimental observation - or at least most of them!!

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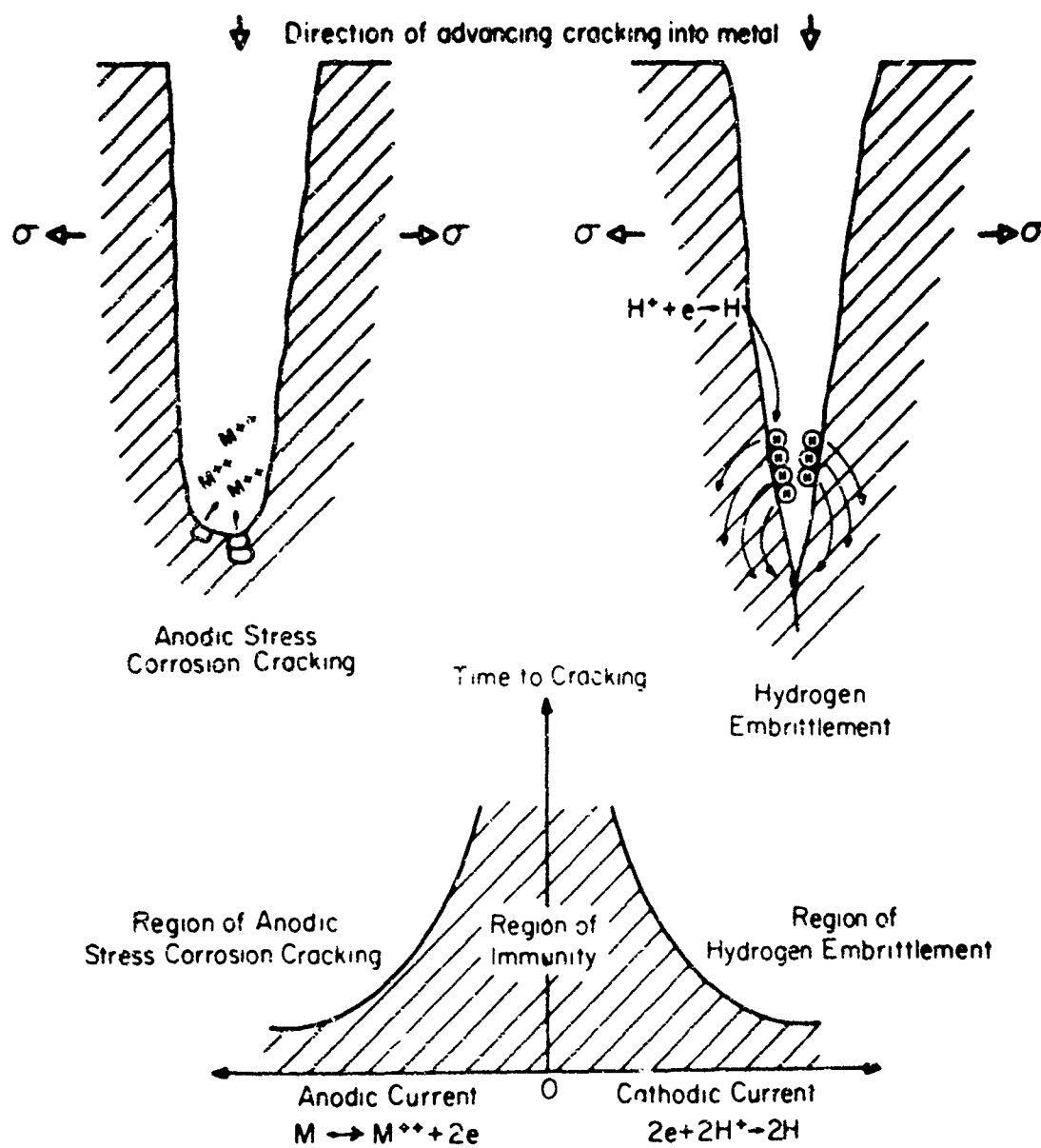


Fig. 1 Schematic differentiation of anodic stress corrosion cracking and cathodically sensitive hydrogen embrittlement

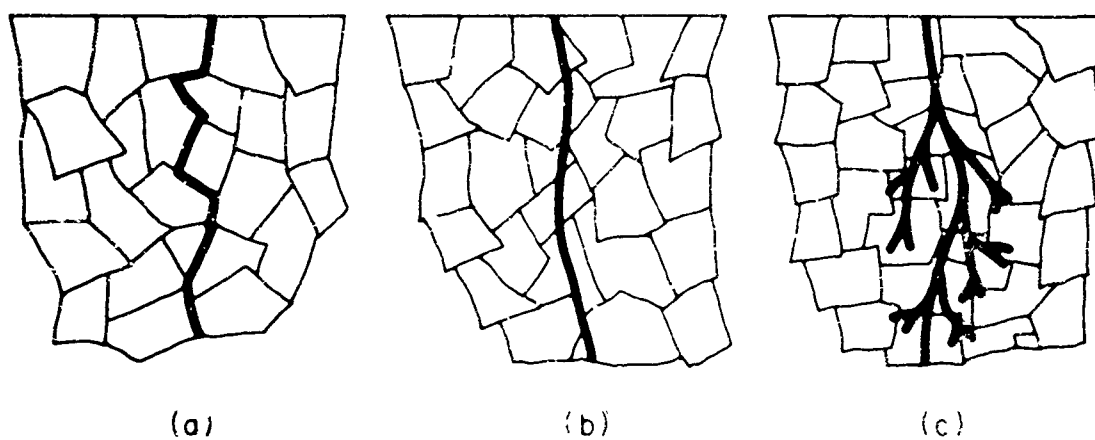


Fig.2 Schematic illustration showing the important modes of environmental cracking.
(a) intergranular, (b) transgranular and non-branching, (c) transgranular
and branching

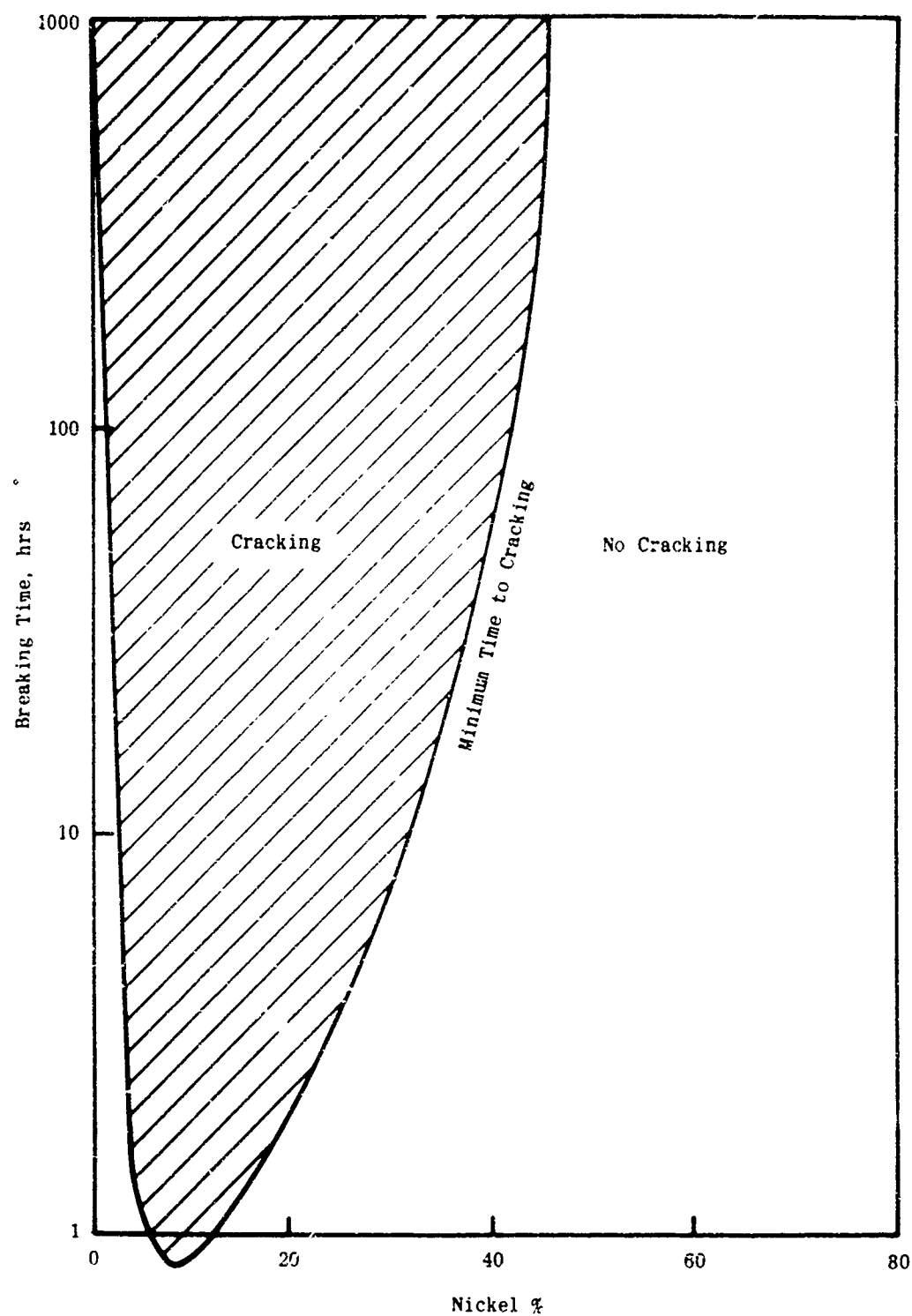


Fig.3 Effect of nickel content in an iron-18 chromium base on stress corrosion crack in boiling MgCl_2

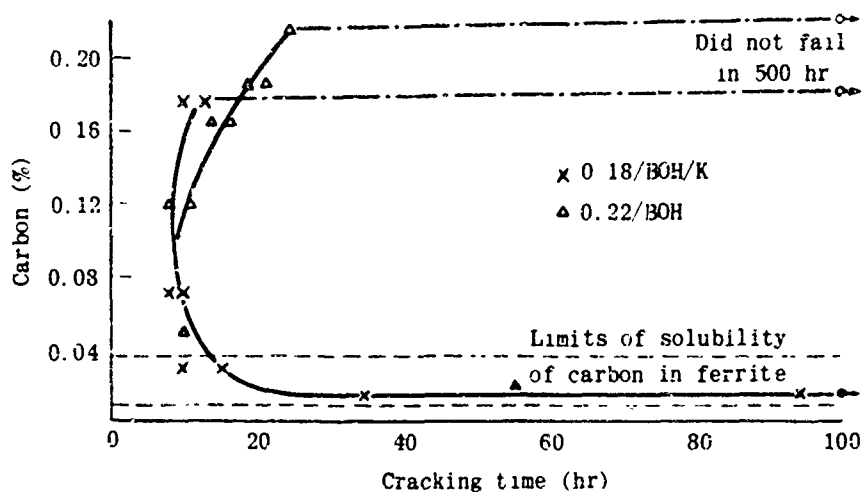


Fig. 4 Effect of carbon content on the cracking time of mild steel exposed to boiling calcium ammonium nitrate

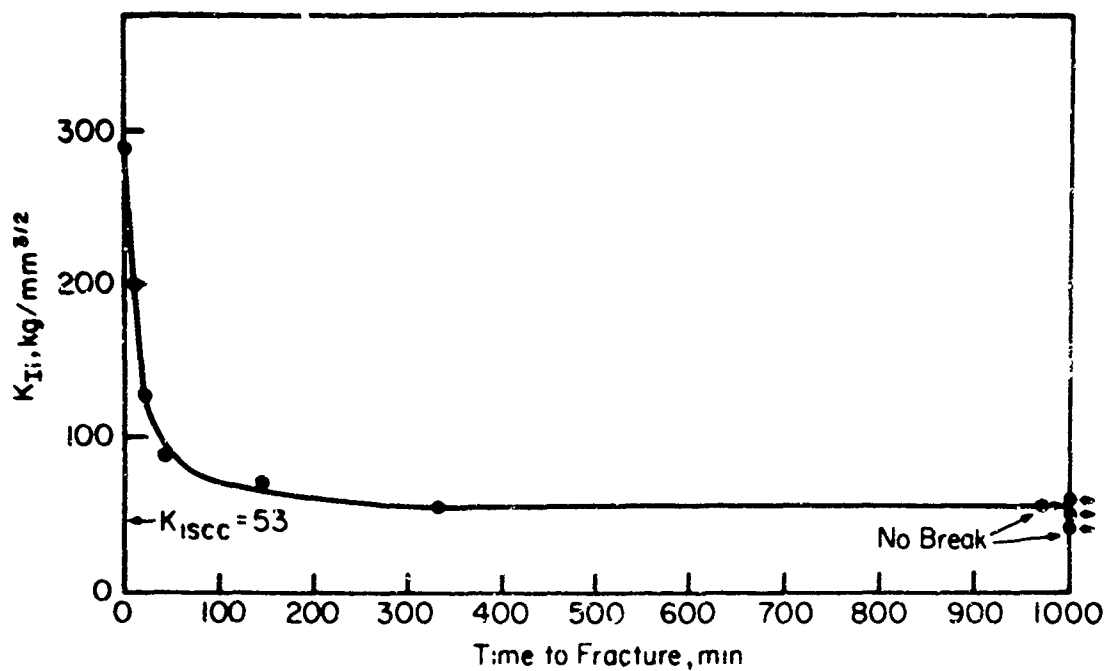


Fig. 5 Effect of initial stress intensity on time to fracture for AISI 4340 steel heat treated to about 210,000 lb/in.² yield strength

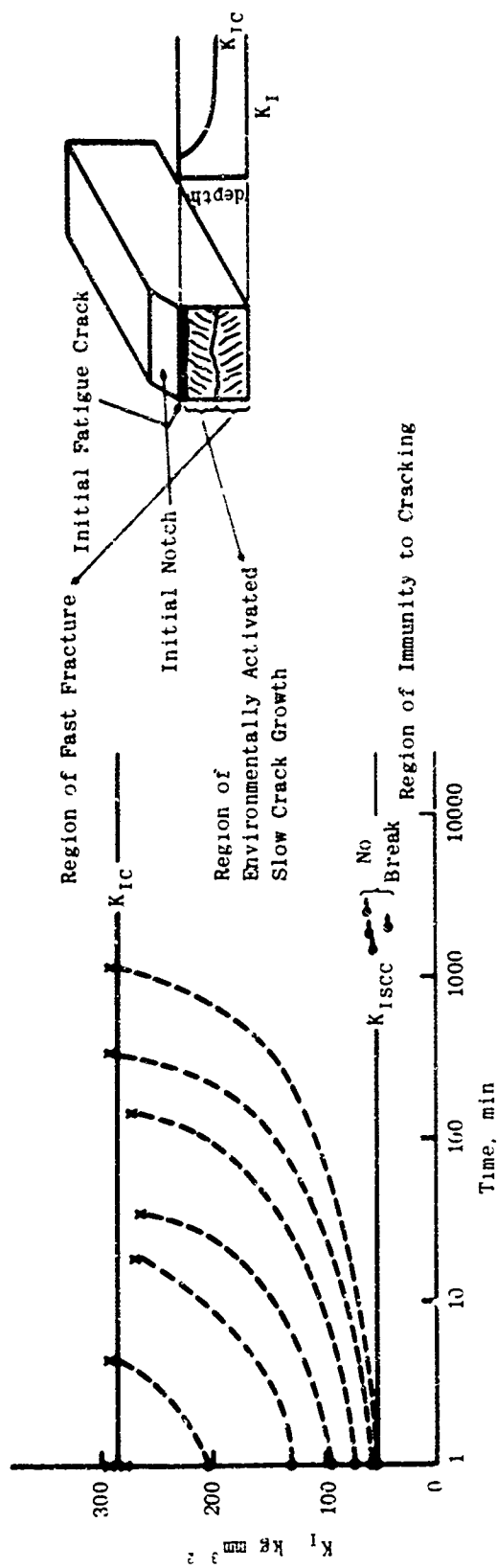


Fig. 6 Same experiments as that in Figure 1 except indicating instantaneous K_I values for beginning of stress corrosion cracking and for onset of fast fracture (K_{IC}). Also shown at right is schematic drawing of fractioned cantilever test bar in which slow crack growth and fast fracture have operated

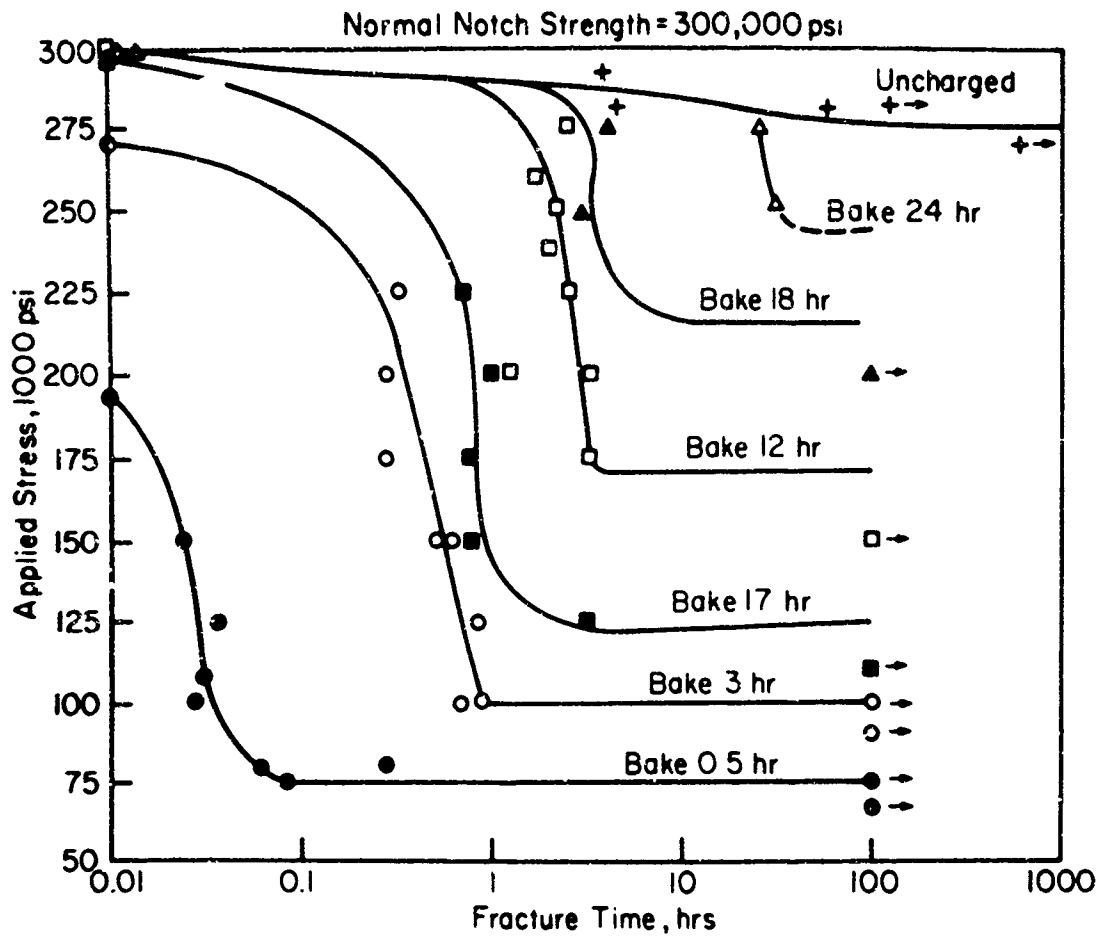


Fig. 7 Static fatigue curves for various hydrogen concentrations obtained by baking different times at 300°F. 4340 steel

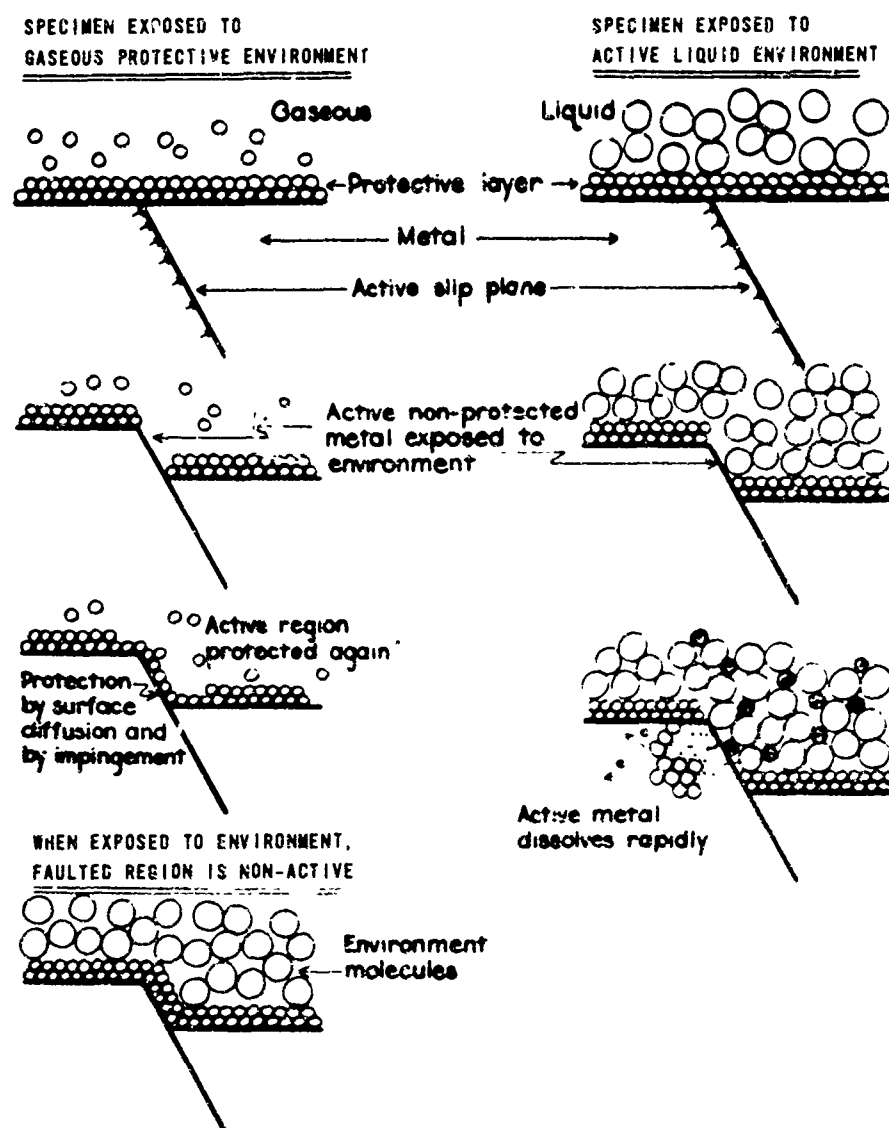


Fig.8 Schematic process of passivation of active slip step shown and compared with rapid attack at non-passivated slip step. Activated region may also be capable of absorbing hydrogen (Ref 1)

DISCUSSION ON PAPER BY M.G. FONTANA

The discussion was concerned with mechanisms of stress corrosion and specificity to certain corrodents.

Professor L. Graf distinguished three types of material:

- (i) homogeneous not supersaturated.
- (ii) supersaturated.
- (iii) materials containing impurities or small additions.

He thought that the mechanisms of SCC would be different in these three classes.

Work at the Max-Planck-Institut at Stuttgart had been in type (i) alloys. Although an increase in concentration of the second alloying element had been found to increase the reactivity of grain boundaries and the reactivity of regions in a state of flow, neither effect was enough to cause SCC; if it were, then all non-supersaturated alloys would be susceptible, which was not so.

It had been shown that SCC only took place if a potential difference was present between crack root and walls, and this difference was great enough only if the walls were cathodically polarised.

The nature of the cathodic layer had been sought. In alloys containing noble metals e.g. Ag-Au or Cu-Au, the layer consisted of a film of the noble metal either left behind after selective solution of the baser metal, or selectively redeposited after dissolution of the total alloy. Thus any corrosive agent not forming complex compounds caused SCC in these alloys. Commercial alloys not containing a noble metal constituent, however, suffered from SCC only if a cathodic layer of corrosion product or passive film formed on the crack wall; susceptibility to SCC was, therefore, specific to those corrodents in which a cathodic layer formed.

Brass was susceptible to SCC in ammonia solutions because the copper tetrammine formed in the primary reaction decomposed to Cu_2O which was deposited on the crack walls to give a cathodic layer. 70Ni-30Cu alloy did not suffer SCC in ammonia solutions because, although copper dissolved, no precipitate formed, in the presence of HF, however, Cu_2O was precipitated and the alloy was susceptible to SCC. It was not easy to predict whether cathodic layers would form and SCC occur in any particular corrodent. If gold were added to commercial alloys, however, then a cathodic film of gold could form and the materials would be certain to be susceptible to SCC.

Mr J.B. Cotton spoke of specificity of material and environment. 70/30 brass was almost as susceptible to small amounts of sulphur dioxide as to ammonia. Not only were corrodents specific, but also their concentrations. Many concentrations of ammonia did not cause SCC of brass, and a sulphur dioxide atmosphere caused it only in the concentration range 0.01 to about 2%. At greater concentrations overall attack occurred and no SCC. Professor Graf commented that attack by sulphur dioxide gave copper sulphate, and that both copper sulphate and copper nitrate gave rise to SCC in brass, the cathodic layer on the crack walls being Cu_2O .

Dr J.C. Scully described his work at Leeds. He was trying to explain the interaction of the metal substructure and the corrosive environment and showed diagrams of a formalised slip step at the bottom of a crack. Susceptibility to SCC depended on the rate of passivation of freshly exposed metal. As well as being reactive to a corrodent, freshly exposed metal could absorb hydrogen readily; in titanium alloys hydride plates had been detected.

Dr P.R. Swann agreed that there was no unique correlation between slip mode and transgranular cracking of single phase alloys because it was not possible to change slip behaviour without at the same time changing other variables, e.g. composition. Nevertheless he believed that slip mode did play a decisive part in SCC because transgranular cracks appeared to nucleate where active slip steps broke protective surface films. Other things being equal, it would be expected that coarse slip (planar dislocation arrays) would do more localised damage to the surface film than fine slip (cell structure).

In Copson's data given in Figure 3 of Professor Fontana's paper, the decrease in susceptibility to SCC as the nickel content (of iron -18% chromium) was reduced below 8% could better be represented by an almost discontinuous change corresponding to the change from austenite to martensite or ferrite, an effect opposite to change in susceptibility to hydrogen embrittlement. Austenite became resistant to SCC when it was transformed by refrigeration to martensite. Although the change in structure could introduce other effects, e.g. in the mechanical behaviour of the metal and the coherency of the protective film, the most obvious effect was the change in slip mode from coarse slip in austenite to fine slip in martensite.

LABORATORY ASPECTS OF ALUMINIUM ALLOYS

by

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LABORATORY ASPECTS OF ALUMINIUM ALLOYS

Dr Hildegard Cordier

1. INTRODUCTION

For aluminium alloys the phenomenon of stress corrosion cracking is observed in AlMg- and AlCuMg-alloys, and especially in the group of high strength age-hardening alloys of the types AlZnMg and AlZnMgCu. Although these alloys have been known in Germany for more than 20 years and find extensive use as constructional materials, especially in aircraft, the true cause of the appearance of stress corrosion cracking is still not yet explained in detail. Work on the problem of stress corrosion cracking is restricted essentially to the alloys of the group AlZnMg. This paper therefore deals with the various opinions on the processes contributing to the stress corrosion cracking of AlZnMg- and AlZnMgCu-alloys, and the consequent metallurgical means for avoiding it.

As an introduction it seems appropriate to point out that with the high strength AlCuMg alloys a form of corrosion damage occurs, the appearance of which cannot be distinguished from the stress corrosion cracking in AlZnMg alloys. The observation that with AlCuMg alloys - as against AlZnMg alloys - material aged at elevated temperatures is less resistant than that aged in the cold gives rise to the opinion that another mechanism is involved. For this sort of intercrystalline disorder, which perhaps should be called "corrosion under stress", probably predominantly chemical or electrochemical processes are in action, while in the disorder described as "stress corrosion cracking" physical-metallurgical processes clearly play a predominant part.

2. TESTING FOR STRESS CORROSION CRACKING
IN A LABORATORY

The actual sensitivity to stress corrosion cracking of a material can best be determined by tests under a fixed load. This form of testing is only not permissible if the specific sensitivity is to be determined, i.e. if, for example various alloys are to be compared or a given alloy to be investigated in various stages of age-hardening. In this case the test should be carried out if possible on recrystallised metal, so that a more favourable structure - with respect to stress corrosion cracking - (cast or extruded structure) does not simulate better resistance. Etching of the test piece before testing gives a uniform surface and reduces the scatter of results. By the addition of 0.5% sodium chromate to the corrosion solution (2% NaCl) the overall corrosion is stopped so that after a long time no falsification of the result is to be feared. If, however, general corrosion occurs, its contribution can be determined by putting a number of test pieces in the corrosive medium without stressing them and then measuring the decrease in mechanical strength.

The percentage proportion of the stress corrosion can be determined from the relationship

$$F = \frac{\text{strength loss by stress corrosion}}{\text{strength loss by corrosion without stress}} \times 100 (\%)$$

due to R.W.Elkington in "Corrosion Testing Procedures" by F.A.Champion (1964).

On the basis of numerous tests it has been shown that the relationship between the test stress and the life of the test piece is best represented by a linear dependence of the test stress on the logarithm of the life.

The former test methods generally used, with constant deformation (loop test, fork test pieces) e.g. in the investigation of a given alloy with various ageing stages, do not give comparable results because the magnitude of the test stress acting on the test piece is in this case much dependent on the strength level of the material being examined. However, with this test method definite service conditions can be simulated, so that it is very important as a test for approximating to practical conditions.

A most simple and rapid, yet very decisive test, which can be used for the qualitative determination of sensitivity to stress corrosion cracking in the short transverse direction is the cut-edge method (Schnittkanten Method). Test pieces of arbitrary dimensions are cut or stamped out. The internal stresses thus produced in the test piece cause splitting or cracking of the test piece from the edges when stored in air, or accelerate in corrosive solution. The cracks extend parallel to the surface of the sheet metal as far into the material as the region deformed by the shearing action and its attendant internal stresses (see Figure 1). Again, the test stress is here dependent on the strength level; this must be taken into account in evaluating the results.

3. CONCEPTIONS ABOUT THE MECHANISM OF STRESS CORROSION CRACKING AND METALLURGICAL MEASURES TO AVOID IT

From investigations by W.Gruhl², it is assumed that stress corrosion cracking proceeds in three stages which are designated as the incubation period, crack formation period and crack propagation period. During the incubation period the influence of the corrosive solution predominates and a chemical equilibrium is set up between the latter and the metal surface. In this way the protective oxide and surface layers are penetrated, so that the necessary contact between metal and solution takes place for initiating the true stress corrosion cracking processes. The duration of this preparatory period can vary. It is dependent on the thickness of the oxide layer. In the alloy AlMg5, for example, an oxide layer rich in MgO is formed so that, especially at high test stresses, the existing sensitivity to stress corrosion cracking of these alloys may be temporarily hidden. If, in laboratory tests, it is required to ascertain the specific sensitivity of the material, then stress corrosion tests in an apparatus under alternating or cycling conditions, the salt-spray test or weathering tests, seem less appropriate, because during the test stable protective oxide layers are formed. These tests, however, have their importance, if the resistance of the material is to be tested in the conditions existing in practice. It is worth noting that with AlZnMg alloys the behaviour to general corrosion has clearly no influence on the resistance to stress corrosion cracking.

Test pieces, which on the addition of sodium sulphite or phosphate were strongly corroded, even partially having inter-crystalline corrosion, showed the same life as test pieces in which the general corrosion was practically completely suppressed by the addition of chromate.

For the crack formation process the simultaneous action of stress and corrosion is necessary. According to the work of A.J. Forty³, crack formation can be imagined such that on the surface of the test piece agglomerations of vacancies are produced by the selective dissolving out of one component, which leads to crack nuclei. H. Nichols, W. Rostocker⁴, F.N. Rhines, J.A. Alexander and F. Barclay⁵ and W. Gruhl⁶ assume, on the contrary, that the effect of the corrosive medium at this stage depends on the reduction of the surface energy necessary for crack formation, so that formation of micro-cracks is facilitated. In any case it seems certain that the processes proceeding during the second stage are appreciably influenced by the concentration of vacancies and arrangements of dislocations in the material.

In the third stage crack propagation takes place. According to A.J. Forty, this short process is determined exclusively by the stress and no corrosion action is involved.

Investigations by W. Gruhl and H. Cordier⁷ have shown that, with the Al/ZnMg alloys, there is a distinct influence of the temperature of age-hardening on the stress corrosion behaviour. In Figure 2 the logarithm of the life is plotted as a function of the test stress for various ageing treatments of an Al/ZnMg3 alloy. It can be seen that the stress-life lines are displaced to fairly long times with increasing ageing temperature. It can be concluded from this that the sensitivity to stress corrosion cracking is here not produced by stable precipitation which occurs at high ageing temperatures, but rather age-hardening states which are formed at low temperatures. Whether here it is a question mainly of coherent or non-coherent precipitation cannot yet be stated. However, that the reverting hardening zones arising at low temperatures unfavourably affect the stress corrosion cracking behaviour can also be proved from the fact that the life of the test piece is raised to an increasing extent after several re-forming and re-hardening stages. Figure 3 shows that the life of test pieces of Al/ZnMg3 which were aged, for example, at 90°C, increases to an extent related to the proportion of existing cold-hardening zones which are broken down.

A further possibility, known for some time, for improving the resistance to stress corrosion cracking is the addition of stabilisers, e.g. Cr, V, Mn (Ref.8) to Al/ZnMg-alloys. The effect of these elements rests clearly on the formation of nuclei, by which the growth of more stable precipitates is facilitated⁹. It may be assumed that the favourable influence which is exercised by delayed cooling - quenching in hot water, or step-quenching - on the stress corrosion cracking behaviour is also to be attributed to the formation of stable precipitates.

This cooling process has the further advantage that the internal stresses present in the material are destroyed to an extent dependent on the reduction of the rate of cooling¹⁰. According to investigations by T. Williams¹¹ on Al/ZnMgCu alloys it has been shown that step-quenching in alloys containing Cr leads to a marked loss of strength. It is, of course, disputable whether to improve the stress corrosion cracking resistance it is more suitable to submit Cr-free alloys to step-quenching or to use Cr-containing alloys which must be quenched quickly.

In Germany Cu-free AlZnMg3 alloys are used only very exceptionally because, despite special heat treatment precautions, there is some improvement but no overall guarantee against stress corrosion cracking is achieved. On the other hand with AlZnMg alloys containing copper it is possible to suppress the sensitivity to stress corrosion cracking by a special heat treatment. More than twenty years ago a method was patented by the Metallgesellschaft in Frankfurt/Main, in which the favourable effect of a two-step (duplex) age-hardening was described. However, this patent was apparently forgotten in the turbulent conditions of the nineteen-forties. Only in 1961 was two stage age-hardening introduced in Germany for AlZnMgCu0.5, in which the material was first heated at 100-120°C and then finally at 160-180°C. With this process the hardening zones produced at low temperatures, which obviously exerted an unfavourable influence on the stress cracking corrosion behaviour, re-formed partially by treating at the higher temperatures. The reduction in strength first occurring here is recovered by further ageing at the higher temperature, in which more stable precipitation zones arise, so that through this treatment a material can be produced which is completely resistant to stress corrosion cracking without having to accept a strength loss. At the same time in the two-stage hardening the internal stresses arising from the quenching are reduced by 30 to 50% (Ref.12).

In America a similar two-stage ageing is carried out under the designation T 73 for the AlZnMgCu1.5. Because of the higher Cu content a rather small loss of strength occurs on re-hardening of this alloy which, however, is accepted as the price for the improved stress corrosion resistance. A.J.Jacobs¹³, on the basis of electron microscope examinations on the alloy 7075, confirmed that the states T 6 and T 73 were differentiated by a network of dislocations which is piled up in the vicinity of large precipitates of M-phase ($MgZn_2$), in the T 6 heat treatment (see Figure 4). These $MgZn_2$ precipitates in the T 73 state are at the grain boundaries and inside the grain. They are dissolved out by the corrosion attack. A.J.Jacobs now assumes that the dislocations near the dissolved-out $MgZn_2$ precipitates lead to crack nuclei, which then propagate under the influence of the stress and cause cracking of the material at the grain boundaries.

At Cambridge University a theory was developed by Thomas and Nutting¹⁴ on the occurrence of stress corrosion cracking in AlZnMg alloys, which has recently been further extended by Nicholson and his colleagues¹⁵. According to this the production of stress corrosion cracking is connected with precipitation-free zones on the grain boundaries (see Figure 5). Figure 6 shows in outline how the crack formation can be represented. Figure 6(a) shows the structure formation before maximum strength is reached. Relatively few fine precipitation zones are present inside the grains and at the grain boundaries are coarse non-coherent precipitates. When a load is applied to the material, the dislocations can therefore cross the grain boundaries without difficulty from one grain into another. In this temper the material is not sensitive to stress corrosion cracking.

At the maximum strength (Fig.6(b)) with the maximum sensitivity to stress corrosion cracking the precipitates within the grains are, on the other hand, very densely distributed and the grain boundaries covered with cohering precipitate fringes, so that in this case the dislocations cannot cross the grain boundaries. Their movement is much more limited to the precipitate-free zone. Under stress, flow and finally rupture of the material should occur. It is, however, not fully understandable that a brittle inter-crystalline stress corrosion crack should arise in an inherently ductile precipitate-free zone.

Of course these conceptions of the mechanism of stress corrosion cracking do not explain the observation that with AlZnMg alloys the maximum sensitivity is after ageing at room temperature (see Figure 1).

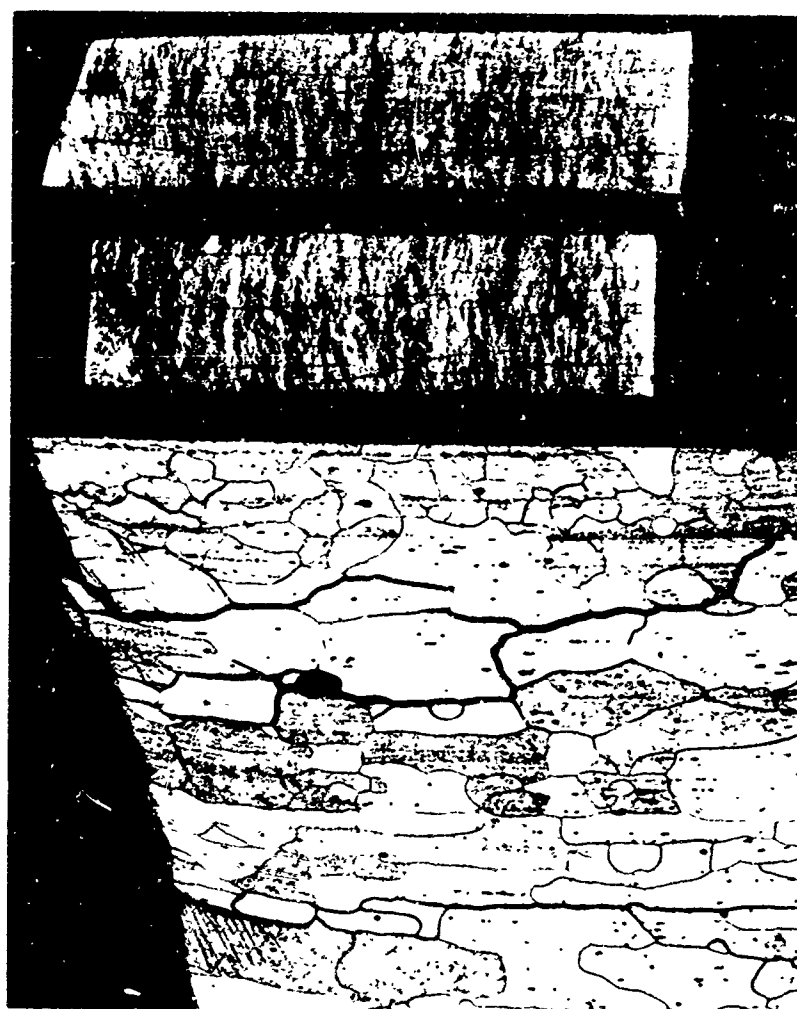
According to investigations by I.J.Polmear¹⁶ in Australia and W.Rosenkranz¹⁷ in Germany, a further, obviously relatively costly, possibility for avoiding stress corrosion cracking consists of the addition of some 0.4% Ag to the AlZnMg and AlZnMgCu alloys. Here the silver addition has clearly an indirect effect. Alloys containing silver, contrary to the case for Ag-free ones, can be directly aged at temperatures of 160-180°C, without loss of strength or need for two-stage ageing. The improved resistance to stress corrosion cracking of the alloys containing silver obviously depends less on the silver addition itself - to improve electrochemical potential - than on the formation of stable precipitates at the higher ageing temperature. Alloys containing silver which are aged only at room temperature are, on the contrary, as sensitive as silver-free alloys.

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Macroscopic
fractograph

Photomicrograph
of structure

Fig.1 Cut-edge method

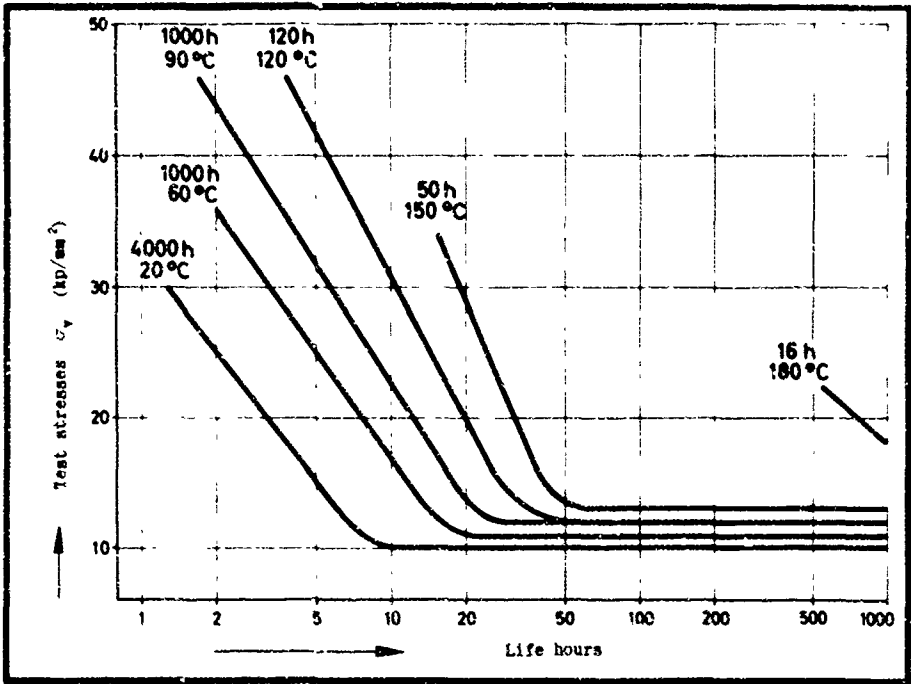


Fig.2 Stress-life curves after maximum hardening at different temperatures

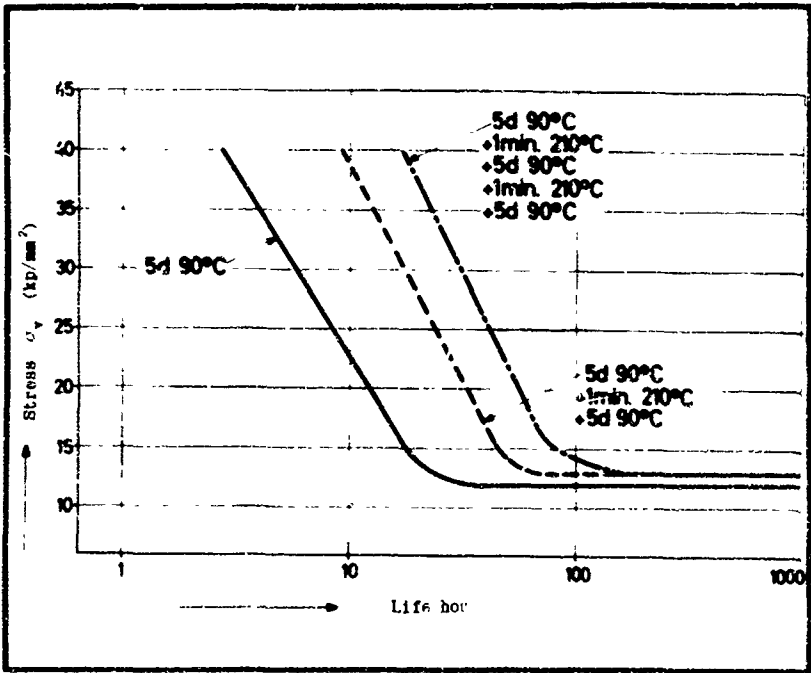


Fig.3 Effect of several re-forming and re-hardening processes on stress corrosion behaviour

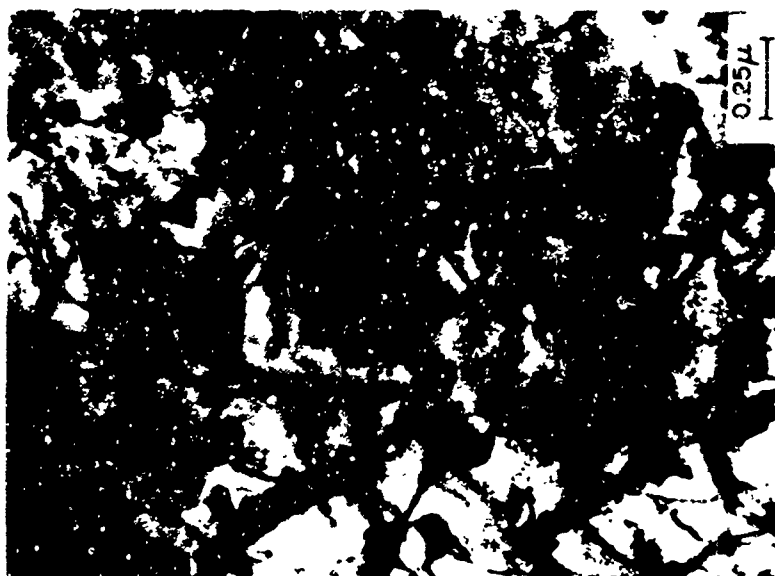


Fig. 4 Alloy 7075 T 6
Dislocations piled up on $MgZn_2$ precipitate
(after A. J. Jacobs, Ref. 13)

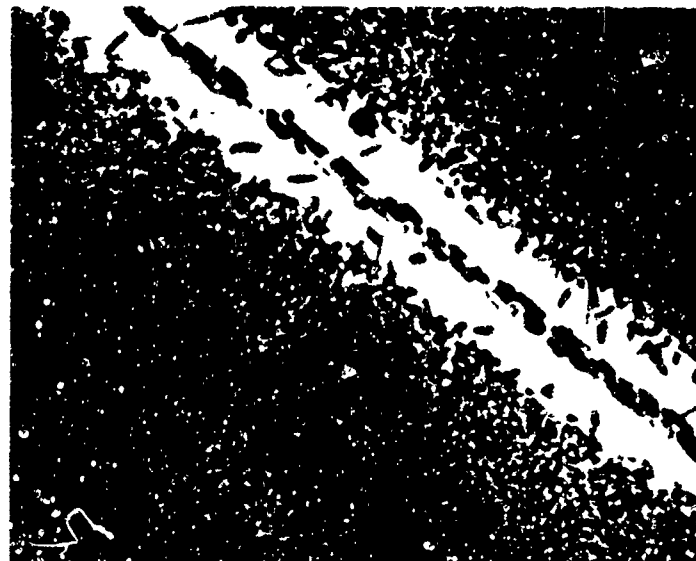
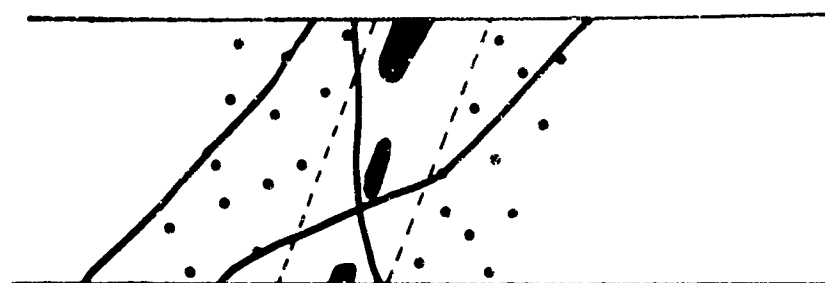
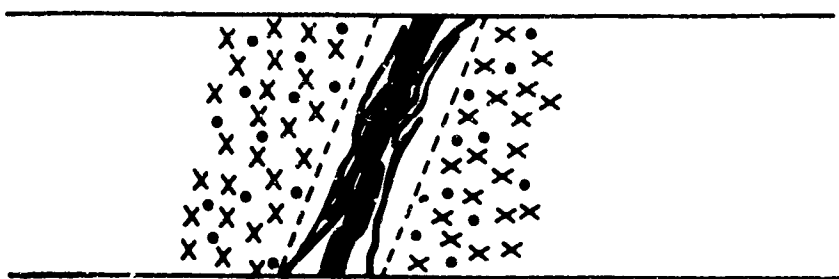


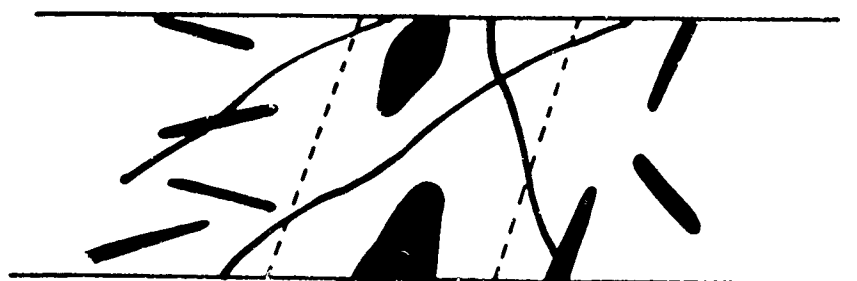
Fig. 5 Precipitate free zone near the grain
boundary (Embury and Nicholson, Ref. 15)



(a)



(b)



(c)

Fig.6 Schematic representation of slip processes

(a) Before maximum hardness

(b) At maximum hardness

(c) After overageing

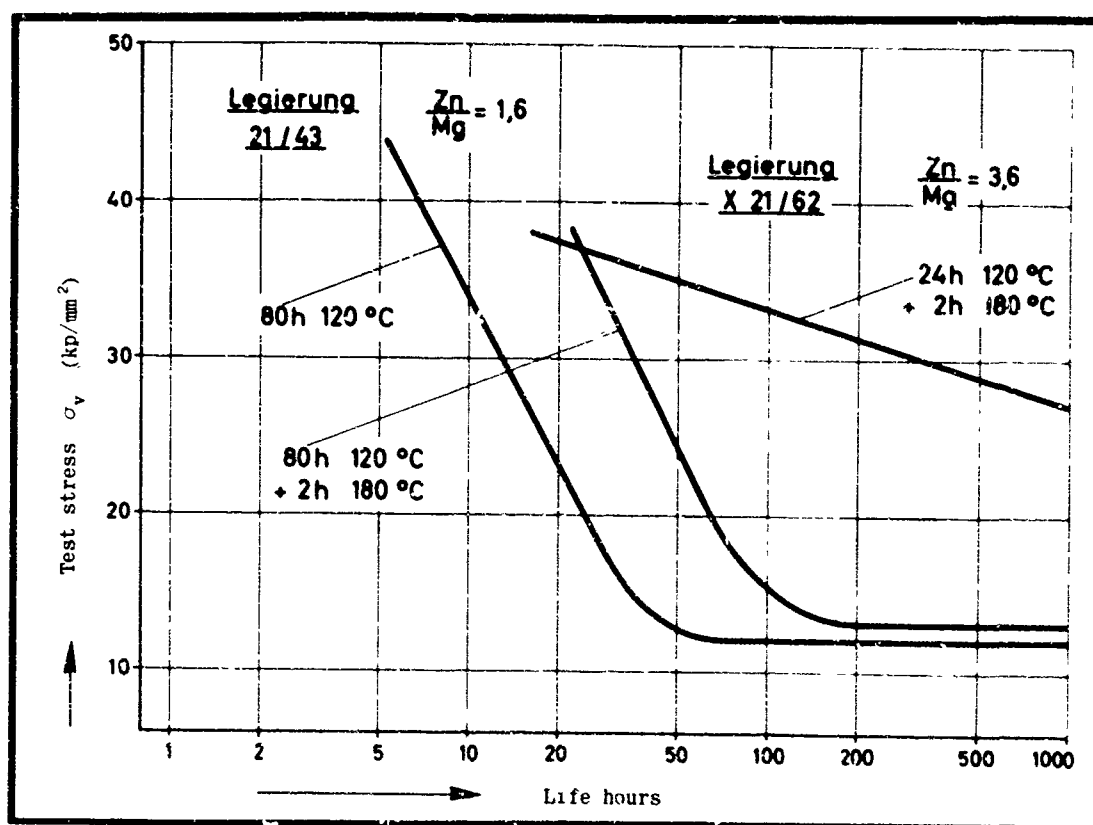


Fig. 7 Stress-life curves for various Al/ZnMg alloys. Total Zn + Mg = 7.5%

SOME ENGINEERING ASPECTS OF STRESS CORROSION CRACKING
IN HIGH STRENGTH ALUMINUM ALLOYS

by

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SOME ENGINEERING ASPECTS OF STRESS CORROSION CRACKING IN HIGH STRENGTH ALUMINUM ALLOYS

J. J. Waller

1. INTRODUCTION

In this paper, I will attempt to present some of the problems, and their solutions, which confront the design engineer when he is concerned with designing structural parts made of high strength aluminum alloys, in an effort to prevent stress corrosion failures from occurring in service. I will also describe some of the factors associated with the manufacturing and assembly operations of such parts - conditions which are beyond the direct control of the designer but which also can lead to service failures. That is, manufacturing and assembly operation abuses are very often the cause of stress corrosion failures in service. Frequently, too, what sometimes appear to be manufacturing and assembly operation deficiencies, are really the result of engineering personnel not furnishing the necessary detailed instructions of procedure to shop personnel. Procedures, in the form of notes on drawings and in process specifications, are either or both, inadequate or too vague for the shop staff to understand what is required to produce a stress corrosion resistant part or assembly.

Since aluminum alloys, in the die-forged form, are most prone to stress corrosion cracking, I will refer to forgings primarily throughout this paper, but the same set of circumstances will apply also to extrusions, plate, and to sheet which is not protected by a coating of pure or slightly alloyed aluminum.

Using the normal sequence of events, from the basic conception of a forging design until the completed unit is assembled to a major airframe component, the problems and decisions to be considered will be discussed in more or less the order in which they arise.

2. DESIGN

2.1 Selection of Material, Stress Corrosion Properties

The designer usually will make a basic drawing layout of the finished part required, encompassing the geometric and structural aspects necessary for the function of the part. He will then consider how the part can be made from a forging using his own knowledge and experience, that of the materials engineer and frequently that of a forging supplier. The stress engineer, of course, also comes into procedure at this time and he will request, generally, the use of an alloy which has the highest mechanical properties available. Since such high strength alloys usually have the lowest resistance to stress corrosion cracking, the materials engineer and stress

III-4

engineer - after much discussion - will arrive at a compromise decision, to use an alloy having the best mechanical and stress corrosion resistant properties.

At this stage, the stress and design engineers have what may be considered to be the easiest task, since the mechanical properties of the alloy selected are usually defined very precisely in a material specification. However, the materials engineer is not so fortunate in making a decision, as there are many sources of information for the stress corrosion resistance properties of aluminum alloys. Some of these sources do not give precise information, others contain information which is based on methods of testing which can be disputed or which cannot be correlated even indirectly to service conditions; still others contain information which would lead one to conclude that this property of aluminum alloys varies almost from laboratory to laboratory. Each laboratory will generally use its own conception of what the corrosion medium and exposure cycle should be. The configuration of the test specimen and the method of stressing are two other variables that are involved in the evaluation. It seems that each laboratory evaluating alloys for stress corrosion resistance has its own method of how this evaluation should be made. The materials engineer has to decide which method should be used in selecting the proper alloy for the application being considered.

In our case, we place a great deal of emphasis on the results of such researches, published by the laboratories of one of the large aluminum alloy producers in the United States. Their work is considered to be done in a very comprehensive manner and by personnel who have gained a reputation of great respect in the field of corrosion. Since they work very closely with the airframe designers and various government agencies who operate aircraft in severely corrosive environments, their research programs are generally related to service conditions, and the results of their research work influence the formulation of alloys.

Where doubt exists, however, or where the operating conditions are peculiar, we sometimes make our own laboratory checks in relation to the particular design we are producing. Even so, as laboratory methods of evaluation cannot be truly correlated with service conditions, the laboratory test results are used only to compare one alloy with another, i.e. they are used on a relative, and not on an absolute, basis.

We then select an alloy with as high a stress corrosion resistance as possible, consistent with mechanical properties which will not give us a severe weight penalty. Since all high strength aluminum alloys have a stress corrosion weakness in varying degrees, certain precautionary measures have to be taken during design, manufacture and assembly to compensate for this weakness, as described below. One exception to the statement just made is the recently developed over-aged temper, which gives the alloy an almost complete immunity to stress corrosion failure. Unfortunately, its mechanical properties are somewhat lower than those of alloys in the conventionally aged tempers and stress and weights engineers are reluctant to use this material.

2.2 Detail Design

When we reach the stage of detail design of the part, every possible step is taken to minimize residual or sustained stresses and to prevent, as far as possible, any corroding medium from reaching the metal. With regard to sustained or residual stresses, we hold the common belief that intermittent service tensile stresses do not contribute to stress corrosion failures, and that only continuous stresses are responsible for failures.

To illustrate how to keep continuous tensile stresses to an absolute minimum and how to prevent as far as possible the corroding medium from reaching the metal, let us assume that we have a part to be machined from a forging to be made of a high strength aluminum alloy. This is to be a large part, having a maximum cross section, in the forging, of about 5 inches in diameter, that the finished part has to have a large blind hole incorporated during machining, and that a number of copper alloy bushings have to be press-fitted into certain areas of the machined forging. Also, the finished part will have a relatively thin flange by which the part is attached to the assembly, by means of both rivets and bolts. I would now like to run through the various operations that are carried out during the detail design, manufacture and assembly for the type of part being considered - again, in an effort to minimize sustained and residual stresses which can exist in the completed part after assembly, and to afford the best protection against corrosion.

2.3 Grain Flow

Firstly, with his own knowledge of forging fabrication and with the assistance of specialist personnel in the field, the designer arranges the layout of the forging with the direction of grain flow being parallel to, or as near parallel to as possible, the direction of principal design stress. Sometimes he has the opportunity to specify the grain flow direction around such areas of the forging as bosses, which will be best for stress corrosion resistance where bushings and the like may be press-fitted into position. Also, he makes every effort to avoid the occurrence of end grain exposure in the surface of the finished machined part, though this is often difficult.

2.4 Inserts

Next, we come to areas in the forging where copper alloy bushings are to be press-fitted into place. Special care is taken to select the magnitude of interference-fit so that the sustained stresses developed by press-fitting do not exceed the threshold stresses for resistance to stress corrosion cracking of the alloy to be used. The dimensional tolerances of the housing for the bushing, and the outside diameter of the bushing itself, have to be very carefully selected. Unfortunately and frequently, the sustained stresses which are developed from press-fitting operations are not amenable to accurate calculation by stress analysis methods - so that often wide assumptions must be made. There is a growing tendency to limit the magnitude of the interference-fit to one thousandth of an inch and to install the bushing with an anaerobic resin to hold it firmly in place. This maximum interference-fit of one-thousandth of an inch, induces a permanent stress of about 7000 lb/in.², which is generally below the threshold stress for failure.

After the final dimensions of the finished part have been decided, a drawing is prepared of the part in rough machined form. To make the optimum use of the residual compressive stresses which are induced during the heat treating operation it is general practice, particularly in the case of large forgings, to rough-machine the forging so that all material possible is machined away before the heat treating operation takes place. This rough-machining is carried out to allow an oversize condition of 1/8 in. on all surfaces except perhaps where severe distortion from heat treating is expected. These particular areas are left at 1/4 in. oversize.

The part is now completely designed and, except for other details which are beyond the scope of this paper, the drawings for the forging and the finished part are ready for release to manufacture the part.

The first step is to order the forging, and in the case of the example we have taken to describe, the forging design has already been discussed with the producer. The forging is ordered to be supplied in the "as fabricated" temper.

3. MANUFACTURE

3.1 Inspection and Rough-Machining

When the forgings are received in the plant, they are subjected to the usual inspection and non-destructive testing operations. One forging is then sectioned in the appropriate areas, to determine whether the requirements for direction of grain flow as defined by the drawing have been fulfilled. If the forgings are found to be satisfactory at this stage, they are then rough-machined to the dimensions prescribed by the drawing.

3.2 Heat Treatment

The next step is to solution heat treat and to age the rough-machined parts. This becomes a critical operation, particularly because of the blind hole in the part previously described. Solution heat treating temperatures and procedures are well established for all the alloys. However, in many cases, quenching techniques are not. To minimize the development of adverse residual stresses and related distortion, and the tendency to crack that can result from the quenching operation, forgings are quenched in water at elevated temperature. Usually, all alloys are quenched at the same temperature. However, some alloys have individually best-temperatures - a situation which is frequently ignored by heat treating metallurgists. In any case, the elevated quenching temperature should be controlled within a comparatively narrow temperature range throughout the quenching cycle. This range is usually $\pm 10^{\circ}\text{F}$.

In our example, the main problem is properly to quench the metal in the blind hole which has been incorporated into the fitting. Normal immersion quenching procedures will cause steam pockets to develop in the hole and this will lead to low mechanical properties of the metal in that area. To overcome this problem, the regular quenching procedure is supplemented by inserting a pipe or nozzle into the hole so that, when the forging is immersed into the water, water at elevated temperature and under pressure is forced through this nozzle simultaneously with the immersion of the foregoing. Internal quenching, quenching fixtures, racking positions and the use of vent tubes, are all extremely important considerations in minimizing or avoiding the development of residual tensile quenching stresses. Unfortunately, each different configuration of part requires a separate investigation for one or all of these factors which are associated with proper quenching. Generally, the technique to be used can be based on a history of experience that one has had with parts of a similar configuration. Frequently, the whole procedure has to be completely developed on a more or less trial and error basis when the part has a shape unusual to the heat treater's experience.

After one of the forgings has been solution heat treated and next sectioned in the areas defined by the drawing to check mechanical test results, ensure that the specified mechanical properties have been achieved. Once this has been ascertained, the production forgings are heat treated in a manner identical to that of first unit.

At this stage, we should have units with a minimum of residual tensile stresses in the surface areas, resulting from heat treating.

The forgings are then machined to finished-size dimensions.

3.3 Introduction of Compressive Stresses

We are now ready to carry out what is considered to be another one of the most important steps in the prevention of stress corrosion cracking and this is to induce, in all surfaces of the part, a residual or sustained compressive stress. This is accomplished by a shot-peening operation. The complete surface, internal and external, is peened except for the walls of holes which are less than 3/4 in. in diameter. Holes smaller than this are surface rolled or are treated by means of a taper-stepped mandrel. Surface rolling is produced by introducing a hardened steel, smooth ball into the hole and forcing it under pressure against the walls of the hole, while being rotated. The diameter of the ball, of course, is somewhat smaller than the diameter of the hole.

Shot-peening will induce permanent compressive stresses of about 35,000 lb/in² when the process is carried out properly. The depth of these stresses will be about three to seven thousandths of an inch. However, these depths can vary considerably, depending upon the shot-peening technique which is used.

After the shot-peening has been completed, the removal of the contamination of the surface of the part by the peening shot is carried out. The peened part is immersed in a solution of about 25% nitric acid for some 25 minutes. After rinsing, the surface is carefully checked by means of a potassium ferrocyanide solution to ensure that all steel contamination has been removed. The removal of this contamination is obviously very important.

3.4 Protection

The next stage in the manufacturing sequence is the application of the chemical corrosion protection finish. For stress corrosion purposes, one of the best finish processes known today, if it is not the best, is the sulphuric acid anodizing process to be followed by sealing in a solution of sodium dichromate. This finish is applied to the completely machined forging.

Following this, the copper alloy bushings are press-fitted into place. Firstly, the outside diameter of the bushing is cadmium plated to minimize galvanic action between the copper alloy and the aluminum alloy - even though the latter has been anodized and sealed.

The outside of the bushings are next thoroughly coated with undiluted zinc chromate primer and press-fitting is then accomplished. The primer also provides a galvanic

insulating medium but, more importantly, creates a seal against the ingress of moisture between the mating surfaces. Further sealing can be provided by having a bevel machined at each end of the bushing so that the primer forms a bead at each of these ends. Again, the importance of avoiding excessive interference-fits of these bushings cannot be over-emphasized. Throughout the years, we have encountered many service failures caused by stress corrosion which resulted from too high an interference-fit between bushing and hole. Sometimes this high interference-fit was created by poorly dimensioned drawings. Generally, it has been due to holes being made too small or bushings made too large in diameter - dimensions which were beyond those permitted by the drawing.

Some companies use a superior method of installing bushings, by means of a heat and chill method. The aluminum is heated to a temperature of about 250°F., while the bushing is cooled to about -30° or -40°F. When bushings are installed by this method, there is a lesser tendency to scrape off any cadmium plate from the bushing and a greater tendency to insure a more complete coat of zinc chromate primer to exist between the bushing and the housing.

We now apply the primer and paint finish system to the part. One of the best systems consists of a wash-etch primer followed by a coat of epoxy-polyamide primer. If the part is a so-called exterior part, where it is exposed directly to the outside environment and also where abrasion resistance becomes a consideration, then one or two top coats of epoxy paint are applied. The two primers mentioned are of the non-leaching type and there is a tendency now for the industry to revert to leaching type primers. Recently, an epoxy primer of the leaching type has been developed and it is being considered for use without a wash-etch primer under it. As for epoxy top coat materials, these produce excellent impermeable coatings which are hard and abrasion resistant. This type of paint makes an excellent finish for stress corrosion resistance purposes but, unfortunately, after it has aged for some period of time, it becomes virtually impossible to remove by using strippers of the type which will not harm aluminum alloys. There is a growing tendency to use polyurethane or acrylic-nitrocellulose paints in such applications.

3.5 Assembly

We now have a part ready for assembly to one of the major components of the airframe. Let us assume that this part, in our example, is an undercarriage attachment fitting and that the loads it transmits are taken into the wing spar web. The fitting is placed in position against the spar web to determine whether its relatively thin, flat attachment flanges make good contact with the spar web. If the fit-up is poor, then the installation bolts and rivets will induce high assembly tensile stresses in the part. If poor fit-up is obtained, then shims should be used to close up any gaps before the bolts and rivets are installed. Installation or assembly stresses, in our experience, are frequently the cause for stress corrosion failures. The bolts and rivets are next installed. Bolts are carefully torqued to avoid the introduction of high clamping stresses - another source of trouble. Prior to the installation of the rivets, the holes into which they are installed are coated with undiluted primer. Bolts are treated in the same manner unless they are to be considered as removable during service. In this case, the holes are zinc chromate primed in the conventional manner and the primer allowed to dry before installation is made.

We now have an assembly which contains minimum sustained or residual tensile stresses and is well protected against corrosion and so, with these two factors under control, stress corrosion failures are not expected. In our experience, when failures do develop in service they are generally due to one or more of the aforementioned stages in processing not being carried out at all or not being carried out properly.

4. FORMING OF SHEET AND EXTRUSIONS

Before closing, I would like to make a brief remark about permanent tensile stresses which are induced during forming of parts made from sheet, extrusions and tubing. So often, parts are formed from these materials without proper regard being paid to the incorporation of such adverse stresses. These can result in stress corrosion failures developing in service. Parts which are to be severely formed should be so formed with these materials in the annealed or in the as-quenched condition. Where this procedure becomes impractical, and the forming has to be carried out with the alloy in the fully-aged temper, then this forming should be carried out while the material is at an elevated temperature of about 300°F. This temperature, when used for a limited time, will not reduce the mechanical properties of the finished part and will go a long way toward avoiding service failures. The definition of what is severe forming, under these circumstances, becomes a thorny matter and most companies have this resolved, provided, of course, that the drawings or the related process specifications quantitatively define severe forming and that production personnel follow the specified procedures.

As for the expense associated with all these processing details, what I have described will be considered by some to be costly - but when the cost of service failures is assessed, the expense of the original processing being done in the proper manner is not important.

DISCUSSION ON PAPER BY H. CORDIER AND PAPER BY J. J. WALLER

(1) General considerations

Mrs S. Ketcham pointed out that certain alloys and tempers in the Al/ZnMgCu 7075 and 7079 series, and in AlCuMg 2024 series suffered intergranular attack only when stressed; many of the failed components examined in her laboratory had clearly failed by SCC although the metal showed no susceptibility to intergranular attack in a standard unstressed laboratory test. Experiments on AlCuMg alloy quenched at different rates and then aged at room temperature showed intergranular attack only with applied stress if the quenching rate had been fast ($200^{\circ}\text{C}/\text{sec}$ and less) but showed such attack even in the absence of stress at slower quenching rates ($70^{\circ}\text{C}/\text{sec}$ and less). In the former case, no active path existed until stress was applied. An electrochemical effect due to stress must be postulated to explain initiation of the crack and embrittlement at the root of the crack. The mechanism of these effects was not known and further work was needed.

Mr A. Cibula said that work on Al/ZnMg alloys at the British Non-Ferrous Metals Research Association supported the idea that susceptibility to SCC was associated with stress concentrations at defects, the defects being those introduced into the metal during casting and processing. Susceptibility to SCC was highly directional, but not all the directionality could be attributed to grain shape. A material with good resistance in the short transverse direction could have a ratio of lives-to-failure in the longitudinal: short transverse directions of $10^2:1$, but in a material of poor short transverse properties, the ratio could be 10^3 or $10^4:1$. If recrystallisation was allowed by omission of Cr or Mn, resistance to SCC fell, but not to the short transverse level. Resistance in the short transverse direction varied from batch to batch of metal. Some of this variation could be attributed to inherent notches due to porosity in the metal which had survived working. Experiments in which the freezing rate of the original cast metal was varied by several magnitudes had shown that freezing rate affected residual porosity and, after forging, the transverse ductility and resistance to transverse SCC, the latter over a range of 60:1. If shrinkage porosity or gas porosity were introduced deliberately, the resistance to short transverse SCC was reduced. Annealing helped to reduce porosity effects. So residual porosity as well as grain structure was important.

In relation to this part of Mr Cibula's comments, Mr Goldberg asked whether there was a non-destructive test method which could detect harmful microporosity? Mr Cibula replied, no, the micropores were too small to be detected by present methods. One could only adopt casting and processing procedures designed to eliminate microporosity. Mr Waller suggested that the metal should be vacuum melted.

Mr Cibula went on to say that considerations of microporosity did not throw light on the metallurgical causes of SCC. Although the depletion of solute at grain boundaries was associated with resistance to SCC, any correlation in detail was difficult. In the four Al/ZnMg alloys: high Cu, Cr, high Cu, Mn, low Cu, Cr, and low Cu, Mn, reduction of rate of quench from solution heat treatment reduced the strength and increased the width of the depleted zone at the grain boundaries. The effect on resistance to SCC, however, varied; the high Cu, Cr alloy lost resistance but the remaining three alloys showed little change. Thus large variations in resistance to SCC did not always correlate with variations in microstructure.

Dr E.A. Fell thought that stress corrosion tests should be made not at uniform loads but at uniform proportions of the tensile strengths. It was also unjustified to carry out tests on recrystallised material; as much benefit could be obtained from optimum macro grain structure as from optimum heat treatment. He thought the importance of pure electrochemical effects had been exaggerated. It had been shown that the nature of the precipitate at grain boundaries depended on the orientation between grains; on high angle boundaries, which predominate in equiaxed structures, the precipitate particles were numerous and small and nearly formed a continuous film, whereas on low angle boundaries, which predominate in fibrous structures, the particles were few, large, and widely spaced. These observations would suggest that fibrous structures should be more sensitive to SCC than equiaxed, whereas the opposite was true. It was concluded that SCC properties could not be explained purely in terms of electrochemical effects.

Mr J. Boraston remarked that Dr Cordier's plots of applied stress against log time-to-failure were not of a standard shape, so no prediction of lives was possible. He then presented an analysis of stress corrosion life data which gave a straight line when stress was plotted against the reciprocal of the square root of the time. Straight lines had been obtained from outdoor tests on AlZnMg specimens stressed at from 90% down to 10% of the 0.1% PS, the duration to failure at 10% being ten years, and from many other test data including brasses, martensitic and austenitic stainless steels. Some tests on painted specimens had given a curve, but if a constant induction time believed to represent the time to breakdown of the paint, were subtracted from the total time to failure, then again a straight line was obtained. Plots of Hawkes' results on AlZnMg alloy (J. Inst. Metals August 1964) were shown. Results from specimens containing low internal stresses gave a straight line passing through the origin; those with surface compressive stresses of 6 to 8 tons/in² gave a straight line cutting the stress axis at plus 6 tons/in²; those with surface compressive stresses gave a similar straight line also cutting the stress axis at plus 6 tons/in², not on the negative side as might have been expected.

Mr Boraston put forward this principle with some diffidence. If valid, it would allow a calculation of the long lives at low stresses from quick tests at high stresses.

(ii) Behaviour of particular alloys in relation to heat treatment

Madame Vialatte did not agree with Dr Cordier's distinction between the behaviour of AlZnMg and AlCuMg alloys. Both classes of alloy, and also the AlCuNi type, could be made resistant to SCC by overageing. Madame Vialatte quoted some results on AU4G1 (2024 type), short transverse specimens stressed at 80% of the 0.2% PS under intermittent immersion in 3.5% sodium chloride solution buffered at pH8. Specimens aged at room temperature broke in six days, those aged for sixteen hours at 170°C broke in ten hours, and those overaged for twenty hours at 190°C did not break in thirty days. Overageing caused a loss in mechanical properties of 2 to 5% from the maximum obtainable. Dr Cordier said she had based her conclusions on the finding that artificial ageing improved the resistance of AlZnMg alloys to SCC, but reduced that of AlCuMg alloys, but admitted that her programme of work had not been large. Mr Waller, however, warned Madame Vialatte about comparing AlZnMg and AlCuMg solely on chemical composition. Metalurgical form was also important. When both types were conventionally aged, forged AlZnMg showed greater resistance to SCC than forged AlCuMg, but in sheet form the AlCuMg was superior.

Mr W.M. Imrie could not agree with Dr Cordier's statement that AlZnMg0.5Cu alloy could be made completely resistant to SCC without loss of mechanical properties by step-ageing at 110°C and then 170°C. He had found improvement, but not complete insensitivity, and a lowering of mechanical properties by 15%, the same loss as was caused by the T73 temper on the 1.5Cu alloys. He favoured the chromium-free alloy quenched in boiling water to give low internal stresses, followed by step ageing, twelve hours at 130°C, then sixteen hours at 150°C which gave high resistance to SCC and very little loss of mechanical properties. The second ageing treatment could be given, on return from service, to parts originally given only the single ageing.

Table A-I listed the mechanical and SCC properties of transverse test pieces cut from aircraft forgings and aged by the standard single procedure (SA) and by double ageing (DA). The thickness of the forgings at the heat treatment stage was two to three inches. The specimens were tested outdoors at 90% of the 0.1% proof stress. The results showed an increase in life from the double ageing of at least seven times. A similar improvement had been shown in accelerated laboratory tests.

TABLE A-I

Transverse Samples Extracted from Landing Gear Forgings

TEST	AGE	E		R		A %	ATMOSPHERIC STRESS CORROSION LIFE (DAYS)
		Kgp/mm ²	tons/in ²	Kgp/mm ²	tons/in ²		
1.	SA	46.2	29.3	51.6	32.8	6.0	11
	DA	45.1	28.7	49.5	31.3	5.0	104
2.	SA	48.5	30.8	52.5	33.3	7.0	12
	DA	46.3	29.4	49.8	31.7	4.0	117
3.	SA	46.6	29.6	49.2	31.2	-	13, 28
	DA	45.9	29.1	49.5	31.3	-	136U, 136U, 136U
4.	SA	47.0	29.9	52.4	33.2	4.5	15, 16, 16
	DA	45.1	29.2	51.1	32.4	4.5	108U, 108U, 108U
SA = SINGLE AGED - 12 HR AT 130°C DA = DOUBLE AGED - AS ABOVE + 16 HR AT 150°C SPECIMENS STRESSED AT 90% OF 0.1% PS							

Mr Imrie went on to defend the chromium-free alloy. He had yet to see any evidence that chromium was beneficial in large forgings. In thin walled components, the low internal stresses resulting from the boiling water quench which could be given to the chromium-free alloy outweighed other considerations. Mr Waller, referring presumably to components made before recent advances in quenching and ageing techniques, said that Canadian experience had been that the 7075 chromium bearing alloy had much greater resistance to SCC than the British DTD 683 chromium-free alloy. Mr Imrie remained adamant. He referred to a new American alloy X7080 claimed to be quenchable in boiling water to give low internal stresses, with high resistance to SCC. This was being

achieved, apparently, by replacing chromium by manganese. If this were true, we were back to the DTD 662 which had been in use in the UK since twenty five years! Mr W.K. Boyd said X7080 was a proprietary alloy about which no details had yet been released.

Professor W. Gruhl said that Dr Cordier's statements applied at Al/ZnMg alloy containing 0.8 to 1.0% Cu. Step ageing was only effective on the 7075 type of alloy; it was largely ineffective on low zinc, high magnesium, low copper alloy. He had five years experience with hydraulic tubes with no failures. He believed chromium was necessary and feared to omit it. Although chromium-free alloys could be cooled slowly, he was not sure of their resistance to SCC.

Mr Imrie spoke finally of the silver bearing alloys. Although their resistance to SCC was high, they were sensitive to the temperature of the water quench, and best mechanical properties could be obtained only by quenching in cold water; this led to high internal stresses.

Mr G.B. Evans doubted whether the mechanism of SCC in Al/ZnMg and Al/CuMg alloys was different. In his own work on cast materials, he had found the resistance of both Al-10% Mg and Al-4% Cu alloys to SCC to be much greater in the naturally aged condition compared with the artificially aged. There were practical differences between forged Al/ZnMg and Al/CuMg alloys; Al/CuMg alloys were not used for such intricate parts, and had a much lower rate of crack propagation, so cracks could be detected in time during servicing.

(iii) Selection, manufacture

Mr G.B. Evans doubted Mr Waller's statement that in a selection of materials the stress and design engineers have the easiest task, because mechanical properties were defined precisely in specifications. He thought choice was often governed by properties not quoted in specifications. Mr Waller said his paper had not, of course, covered mechanical properties or resistance to corrosion fatigue, which also influenced the choice of material.

Mr Evans supported the sort of precautions so clearly described by Mr Waller. Concerning rough machining, however, he left dimensions only 1/16 in. (1.6 mm) oversize, one half of that left by Mr Waller; any distortion after heat treatment was corrected by shot peening. He did not believe that a nitric acid dip was effective in removing iron contamination after peening; he always blasted with alumina. Mr Waller adhered to 1/8 in. (3.2 mm) oversize machining as necessary to allow for distortion; one could not always shot peen back to shape. He granted a tendency nowadays to use glass bead peening instead of nitric acid. He thought alumina was too sharp, but Mr Evans said that it had been shown to have no deleterious effect.

Mrs S. Ketcham questioned Mr Waller's claim that chromate sealed sulphuric acid anodising was the best protective treatment. In some stress corrosion tests in the short transverse direction she had found that this treatment delayed initiation but accelerated propagation. Mr Evans always used chromic acid anodising for good protection and detection of grain flow. He saw no difference in protective value between sealed sulphuric anodising and chromic anodising against either corrosion or stress corrosion. Mr Waller continued his support of sulphuric acid anodising. The anodic film was three times as thick as that from chromic acid anodising, it absorbed dichromate sealant much better, and the protection given was at least as good.

On paints, Mr Evans believed in the value of leachable chromate primers; for top coats, polyurethanes gave no better protection than epoxys but had excellent gloss retention and resistance to fluids. Mr Waller thought epoxy top coats best, followed by polyurethanes and acrylics, all being better than nitrocellulose.

(iv) Behaviour in service

Mr Evans pointed out that materials which showed similar resistance to SCC in the laboratory sometimes behaved quite differently in service. Laboratory work on SCC was usually conducted at high stresses which gave relatively short lives to failure, but an aeroplane might have a life of fifteen years. What was needed was not an extension of life under high stresses from a few days to a few weeks but a raising of the threshold stress below which SCC would never occur.

Squadron Leader R. Vernon put the user's case with some force. Two case histories were shown. In the first, an undamaged component, similar to one in another aircraft which had failed by SCC, was cut in preparation for destructive examination; the two halves sprang apart and sideways. In the second, a small crack in a component removed from an aircraft propagated several feet in a week while the component was standing on the hangar floor. Both examples testified to the high level of internal stresses in the components. It was generally agreed, he said, that SCC of aluminium alloy forgings was caused by internal stresses rather than by applied loads. While not denying the value of laboratory work, he wanted a convenient non-destructive test for internal stresses which could be used as a final inspection which would prevent potentially dangerous components being installed in an aircraft at all.

ENGINEERING ASPECTS OF STRESS CORROSION FAILURE
IN MARTENSITIC STEELS

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SUMMARY

The engineering aspects of stress corrosion failures in steels are discussed with particular emphasis on the delayed failures which occur in high-strength steels (yield strengths above 200,000 lb/in²) exposed to water-containing environments. Considering a variety of laboratory methods for evaluating stress corrosion behavior in high-strength materials, the use of pre-cracked specimens represents the most effective test technique. The presence of the pre-crack decreases the failure time and provides optimum sensitivity and reproducibility. In addition, linear elastic fracture mechanics methods can be applied to analyze the failure data and provide a quantitative indication of expected failure characteristics in actual components. In a given class of steels, the susceptibility to stress corrosion as measured by time to failure, can be correlated with the basic fracture toughness of the material. This results from the fact that the stress corrosion crack has to grow a longer distance in a tougher steel before fracture occurs.

In high-strength steels, environments such as dry hydrogen or inert gases containing water vapor can produce delayed failure. The rate of crack growth under these conditions is directly proportional to the applied stress intensity parameter. Shot-peening and coatings have been used to alleviate the tendency for stress corrosion cracking, however, these methods can produce inconsistent results and must be thoroughly evaluated for each engineering application.

ENGINEERING ASPECTS OF STRESS CORROSION FAILURE IN MARTENSITIC STEELS

E. A. Steigerwald

1. INTRODUCTION

Although the ability of an environment to degrade the load-carrying capacity of materials has long been recognized, the optimum methods for evaluating this phenomenon, the application of the results to design situations, and the definition of the mechanisms which produce it, still remain as important material problems. Until recently, the majority of effort in the study of environmentally-induced crack initiation and propagation in ferrous metals has been centered on the stainless steels where combinations of corrosive solutions and stress produce a very significant decrease in the service life of components. With the current application to aerospace structures of high-strength steels which can be extremely susceptible to brittle crack propagation, the importance of environmental effects to service performance has become significant.

Environmentally-induced, stress corrosion fractures^{*} are often difficult to quantitatively evaluate from a design and mechanism standpoint since all the complexities present in fracture are superimposed on the stress corrosion behavior. Within the past five years, considerable improvements have occurred in the methods of designing against brittle fracture by the application of linear elastic fracture mechanics concepts. This approach provides considerable insight into the effects which geometrical variables contribute to the failure process and allows a more rigorous interpretation of the environmental effects. Since the stress corrosion process is unique to a specific material-environment couple no one mechanism is probably applicable to all cases. A compilation of some of the environments which are known to produce stress corrosion cracking in non-stainless steels is presented in Table I. In most cases the stress corrosion phenomenon occurs in systems where general corrosion is very slight. In fact in cases where extensive general corrosion does exist, the rate of stress corrosion cracking is often decreased since the general corrosion process serves to blunt the crack tip.

The purpose of this presentation is to summarize the engineering aspects of stress corrosion failure in steels which are not the stainless grade. The primary emphasis will be placed on the delayed failures which occur in the martensitic type of high-strength steels (yield strengths above 200,000 lb. in.²) in environments containing water or water vapor. These systems are particularly susceptible to catastrophic failures due to brittle crack propagation and represent an important class of engineering problems in which environmental effects are extremely critical.

* In this paper the term stress corrosion will be used to generically describe failures that occur as a result of the combined effects of stress and a specific environment. The use of the term does not necessarily imply that an anodically-induced, electromechanical process is involved.

2. CHARACTERISTIC SERVICE FAILURES

Catastrophic stress corrosion failures in martensitic steels have been reported for landing gear components¹, hydraulic accumulators², and solid-fuel rocket chambers³. In addition, stress corrosion failures in lower strength steels exposed to caustic environments have been observed and studied for the past twenty years^{4,5}. In this presentation the stress corrosion failure of a solid-fuel rocket motor case described by Shank et al. will be used as an example of a typical service failure which is characteristic of the pattern in high-strength steels. The vessel which was 6 ft long, 40 in. in diameter, with a nominal wall thickness of 0.070 in., was made of H-11⁶ high-strength steel quenched and tempered to a tensile strength level of 270,000 lb/in.². The vessel design involved the use of flow-turned cylindrical segments which were joined by welding prior to heat treatment. The closures and attachment skirts were contoured so that no unusual bending stresses were transmitted to the vessel during pressure testing. Following manufacture, the vessel was placed in the test rig and hydrostatically pressurized with water at 70°C. The test sequence illustrated in Figure 1 indicates that the vessel eventually failed at a stress of 185,000 lb/in.² which was significantly below both the design stress and the 216,000 lb/in.² stress attained on the previous cycle. An examination of the fracture origin (see Figure 2) indicated that the failure had originated on the inside diameter from a stress corrosion crack. A series of additional tests conducted on smaller vessels indicated that failure could occur over a range of stress after varying times at the particular stress level and the origin of failure could always be associated with environmental effects. In one test the inside diameter was coated before pressurizing, water was placed on the outside and the failure origin was shifted from the inside to the outer surfaces. In cases where oil was used as the pressurizing medium, no sustained load failures were observed after 435 minutes at 275,000 lb/in.².

Laboratory tests conducted on pre-cracked specimens, shown in Figure 3, indicate the severity of the stress corrosion problem in high-strength steels. Delayed failures can occur in relatively short times at applied stress levels that are less than half of the load-carrying capability in an inert environment. From an engineering viewpoint, the requirement exists for understanding the variables which control the stress corrosion failures in structural steels so that reliable components can be produced.

3. LABORATORY METHODS FOR EVALUATING STRESS CORROSION

A variety of laboratory methods have been used to determine whether specific materials are susceptible to stress corrosion failure and there is little doubt that these techniques can qualitatively define the relative environmental effects. The question arises however, as to what degree laboratory tests can be used to quantitatively determine the actual stress levels and times where delayed environmental failures will occur in actual components.

There are several articles which summarize the methods used for stress corrosion testing^{7,8,9}. The laboratory techniques for applying the stress in the stress corrosion tests fall into two groups - constant strain and constant load. The constant strain is generally developed in a bent beam type system. The apparatus used in this

* The compositions of all the steels referred to in this presentation are given in Appendix A.

method is simple, and exploratory experiments can be carried out in multiple with a minimum of difficulty. In the constant strain test, as cracking proceeds, the stress is automatically relieved; while in the constant load method, the stress increases as the crack develops and the damage rate accelerates. A U-bend, constant strain, type specimen which is also used for stress corrosion studies generally presents a more severe test than the bent beam which is stressed to just below the yield point. The superposition of elastic stress on the plastic strain used in the U-bend specimen usually produces an acceleration of the failure time.

Although the constant load test is somewhat more difficult to perform than the constant strain test, it has particular advantages since the stress is accurately known and the test end point (in terms of failure time) is well defined and occurs in a shorter period of time than in the constant strain methods.

In all stress corrosion tests, an appreciable scatter of results between "identical" specimens occurs. Although the average life is generally recorded, problems exist in using this parameter when specimens remain unbroken at the end of the test period. More recently, the use of the median failure time has been adopted.

Typical data obtained from U-bend and bent beam type tests on high-strength steels exposed to aqueous environments are shown in Tables II and III. Although these test methods are relatively simple to conduct, they suffer from two severe limitations. First, they cannot be used to quantitatively predict service performance, hence they can only be considered as screening tests to define whether one material is superior to another or a particular environment is more degrading. The second limitation deals with the sequence of events leading to stress corrosion failure. In general, this sequence involves the following three steps:

- (a) The surface of the metal slowly becomes pitted by non-uniform corrosion,
- (b) The pit develops into a crack which continues to propagate slowly on a macroscopic basis,
- (c) When the crack attains a critical length with respect to the applied stress, the remaining ligament ruptures by purely mechanical fracture.

In cases where smooth specimens are used to evaluate stress corrosion behavior, the major portion of the failure time involves the formation of the defect which leads to the initiation of the crack. In actual components where complex manufacturing processes are involved, the actual crack initiating defects are often present so that the laboratory tests conducted on relatively small specimens with controlled surface preparation can give misleadingly conservative results of stress corrosion behavior. The drawbacks inherent in the smooth specimen tests can be eliminated by conducting the evaluation on pre-cracked specimens.

The philosophy of using pre-cracked specimens for evaluating material reliability has recently received considerable attention and resulted in many publications in the area of fracture mechanics based on linear elastic theory¹¹. The linear elastic fracture mechanics approach presents a system of analysis which allows a correlation between the many methods of fracture testing and provides a quantitative association between the measured values of fracture toughness obtained in laboratory tests with

the performance of components in service. In practice, this method of fracture analysis assumes:

- (a) that cracks are inherently present in a component
- (b) that a crack is a flat internal free surface in a linear elastic stress field
- (c) that the propagation of the crack is predictable from laboratory tests in terms of the magnitude of the tensile stress surrounding the leading edge of the crack where the separation process occurs.

From stress analysis, the magnitude of the stress elevation surrounding the crack at the instant of failure can be defined in terms of a material constant K_c , which is termed the fracture toughness. Once this material constant is determined, it can in principle be used to predict failure in other systems, provided adequate stress analyses are available. If fracture toughness can characterize failure under tensile loading, then it also has the possibility of serving as a useful parameter for stress corrosion failures since stress elevation at the crack tip is a definitive condition for crack propagation in this type of failure mode.

The determination of fracture toughness as a material evaluation parameter has many advantages, since it eliminates the influence of specimen width and crack size in the evaluation model and provides some measure of the strength characteristics of full-size components. The propagation of a crack, however, in sheet material generally consists of a normal and shear mode. The shear mode which occurs at the free surface, represents a high energy component of crack growth; while the normal, plane strain mode which is present at the specimen center provides a low energy contribution. As the specimen thickness is progressively increased, the contribution of the shear lips becomes a lower percentage of the total energy for crack propagation. As a result, the fracture toughness (K_c) which is related to the energy necessary for crack propagation decreases as the specimen thickness increases. At large thicknesses, the fracture toughness approaches a constant value which represents the plane strain fracture toughness (K_{IC}). In addition, the initiation of slow crack growth in thin-walled components is also governed by the K_{IC} parameter, because the crack first develops as a tongue in the region where plane strain conditions are operative^{12, 13}.

Fracture toughness is generally obtained from one of five basic test methods:

- (a) Tensile test on a pre-cracked sheet specimen.
- (b) Tensile test on a circumferentially pre-cracked round specimen.
- (c) Tensile test with a surface-cracked sheet or plate specimen.
- (d) Tensile test on a single-edge-notch pre-cracked specimen.
- (e) Bend test using a pre-cracked specimen.

A summary of the formulae used to compute fracture toughness is given in Table IV.

In practice, the fracture toughness value (K) is determined from a relatively simple laboratory test and then used to determine the fracture stress in a component provided the appropriate stress analyses and defect size is known for the component situation¹⁴. An example of the method of using fracture toughness for preceding design performance is given in Appendix B.

An analysis of events which occur in environmentally-induced failures indicates the possible advantage of employing pre-cracked specimens and fracture mechanics analysis. In a smooth specimen, exposure of the metal to a corrosive environment can lead to a pit which results in the initiation of a crack and the continued growth of the crack under an applied stress until total fracture occurs. The advantages of testing with pre-cracked specimens have been described by Brown⁷.

1. The time required to initiate environmentally-induced cracking is longer than the time for failure by crack propagation by a factor of about 10^6 . This means that the majority of time in a stress-corrosion test is spent for the initial development of the stress-raiser and an overwhelming bias toward crack initiation is given in the time-to-rupture parameter. In addition, the formation of a pit is often a statistically-controlled event which results in excessive scatter. The use of a pre-crack reduces the scatter and simplifies the analysis of a mechanism.
2. A given combination of environment and alloy may not produce pitting and may therefore indicate immunity in a test of a smooth specimen. If a stress-raiser is present, however, environmentally-induced failure may occur. The delayed failures due to water which occur only in pre-cracked titanium specimens are an example of this phenomenon.
3. The presence of the pre-crack introduces the sharpest possible stress-raiser, hence from an analysis standpoint it results in conservative predictions.
4. The pre-crack provides a stress-raiser which is amenable to treatment by the linear elastic fracture mechanics equations.

The use of fracture mechanics to analyze stress corrosion behavior was first introduced in studies involving high-strength steel sheet specimens⁶. The presence of an aqueous environment on a pre-cracked specimen tended to promote slow crack growth; however, total specimen failure did not occur until crack growth was sufficient to develop the critical value of the stress intensity factor (K_{IC}). This implies that the influence of the environment was present only at the crack tip and the basic toughness of the material was not effected.

In the case of delayed failure on pre-cracked high-strength steel specimens exposed to either distilled water or a 3% NaCl solution, it is believed that characteristic stress intensity parameter K_{ISCC} can be defined below which delayed failure is not observed. Typical delayed failure curves are shown in Figure 4 for the three specimen types illustrated in Figure 3. The use of the pre-cracked specimens along with the appropriate fracture mechanics equation indicates that the minimum K_{ISCC} value determined in the laboratory tests on various specimen configurations is essentially constant¹⁵. On this basis the parameter should be applicable for predicting stresses below which environmentally-induced failure will not occur in components where the maximum defect size is known.

The sequence of events leading to specimen failure in a pre-cracked sample is shown in Figure 6 as a period of environmentally-induced slow growth which is distinguished by fracture appearance from the catastrophic cracking which terminates the test. The degree of slow crack growth that a steel can tolerate prior to total fracture is intimately connected with the basic fracture toughness of the material. For example, in

a steel tested above its transition temperature, the stress corrosion crack must grow a relatively long distance; while at a comparable value of applied stress, a steel tested below its transition temperature would fracture in a very short time. The tough steel may actually have a stress corrosion rate which is considerably greater than the brittle steel, but the time to failure would mask this effect and indicate that the brittle steel is more susceptible. The significant point is that a relatively brittle steel may produce a lower time to fracture in a corrosive environment, not because it is more susceptible to the environmentally-induced cracking process, but because it is mechanically less tolerant to a given crack length.

In a given class of materials which have comparable stress corrosion susceptibility, the total failure time should therefore be related to the basic fracture toughness of the material. A general correlation of this type is shown in Figure 7, where the fracture toughness is expressed in terms of the ratio of the notched tensile strength in air to the unnotched tensile strength in air¹⁶.

It should be emphasized that a correlation between fracture toughness and time to failure in a stress corrosive environment may not always be present¹⁷. Since the failure process in a smooth specimen is composed of pitting, slow crack growth, and ultimate failure, the correlation should only exist in a given class of steels where the tendency for pitting and rate of environmentally-induced slow crack growth are approximately constant. An example would be a given steel tempered to different strength levels or a class of steels, such as the low alloy martensitic, where only relatively small variations in chemistry occur. Under these conditions the correlation between fracture toughness and time to failure is a natural consequence of the fact that the crack must grow longer distances before total failure takes place. In pre-cracked specimens where the time to form a pit is not a major factor, the correlation is even more obvious.

Sufficient data are available on certain high-strength steels like 4340 so that a comparison between the bent beam specimen without a pre-crack, and pre-cracked tensile specimen is possible. Table V lists the comparative failure times for these two specimen types exposed to a distilled water environment. The results indicate that the pre-cracked specimen produces less scatter and considerably lower failure times. In principle, the pre-cracked specimen forces the stress corrosion process to occur, at a localized area at the crack tip, and therefore substantially reduces the scatter caused by the probability effects involved with initiating a crack over a relatively large specimen surface area.

Although the specific selection of a test method often depends on the particular application conditions, the use of pre-cracked specimens has the advantages of increased sensitivity, improved reproducibility and the possibility of quantitatively predicting design performance from the laboratory determined fracture toughness parameters.

4. EFFECT OF ENVIRONMENT

In the case of high-strength steels, aqueous environments with and without chloride additions have received the greatest degree of attention. In pre-cracked sheet specimens, the use of a 3N NaCl solution produced failure times comparable to distilled

water (see Figure 8); however, tests on plate material tested as pre-cracked beams indicated that the distilled water environment was more aggressive than the chloride solutions (Fig.9) (Ref.18). Similar results were obtained on conventional sheet beam specimens tested without a pre-crack. Although aqueous, saline, halogen and caustic environments are the most aggressive from the standpoint of promoting stress corrosion in steels, seemingly innocuous atmospheres such as alcohols can cause environmentally-induced failures in susceptible steels, such as 300M (Ref.6). Failure times produced by several liquid atmospheres on 300M steel pre-cracked specimens are summarized in Table VI. A broad correlation has been observed between the solubility of water in the particular environment and its ability to promote corrosion cracking¹⁹, which suggests that water or a constituent formed by the metal-water corrosion is actually the critical specie in each case.

In addition to liquid environments, gaseous atmospheres have the ability to produce severe stress corrosion effects. Figure 10 indicates that moist argon produces delayed failure in high-strength steel in the same time as a distilled water environment¹⁶. The crack growth curves shown in Figure 11 illustrate that dew points as low as -7°F (less than 1 grain of water per cubic foot of air) are capable of producing stress corrosion of 4340 steel heat treated to a 280 ksi* tensile strength level. The most comprehensive study of the effect of a gaseous environment on the stress corrosion of high-strength steels has been performed by Johnson and his co-workers^{20, 21}. In these studies dry hydrogen at one atmosphere pressure produced failure in pre-cracked tensile specimens of H-11 steel in times that were substantially less than those produced in a distilled water environment (see Figure 12). The results indicate the strong effect that hydrogen has on the crack propagation process. In fact, the addition of oxygen or water vapor to the dry hydrogen resulted in an increase in the failure time. Using crack growth behavior shown in Figure 13 as an indicator, the rate of environmental-crack extension was decreased when oxygen was added to a humidified nitrogen environment until a sufficient oxygen content was reached where stress corrosion cracking in the humidified nitrogen environment was eliminated. The removal of the oxygen and the re-application of the humidified nitrogen resulted in a continuation of the cracking phenomenon. Humidified argon produced behavior comparable to humidified nitrogen. Crack growth rates decreased when oxygen was added, presumably as a result of the formation of a protective oxide film and increased with increasing humidity until a value of approximately 60% (Fig.14). At this point it is believed that the water condenses at the crack tip so that further increases in humidity result in no additional increase in crack growth rate. The crack growth rate has been found to be a linear function of the stress field parameter (K) (see Figure 15) for pre-cracked specimens of H-11 steel exposed to moist air. A knowledge of the relationship between crack growth rate and stress field parameter has been used to formulate a method for predicting the failure time in simple specimen configurations²².

In liquid environments, increased temperatures lead to an increase in the stress corrosion susceptibility. The crack growth rate in high-strength steel is shown as a function of water temperature in Figures 16 and 17. An activation energy of approximately 9000 cal/mole was observed for the failure process. If the atmosphere is liquid or if the gaseous atmosphere is saturated with water vapor, the crack growth rate varies exponentially with temperature; however, if the relative humidity is low and the absolute humidity constant, the crack growth rate is relatively insensitive to temperature²¹.

* kips/in.² = 1000 lb/in.².

In certain engineering components, notches rather than pre-cracks may be exposed to the environment. Under these conditions, the environmentally-induced failure time is increased. As shown in Figure 18, the degree of increase in the failure time is comparable to the increase in the notch tensile strength as measured in air. The results indicate that crack-like defects in the surface of a component can lead to severe stress corrosion susceptibility and the primary contribution to the failure time consists of the time required to nucleate the crack.

5. EFFECT OF STEEL TYPE

The relative susceptibility of various high-strength steels to stress corrosion failure, as measured by bent beam specimens, is summarized in Figures 19 and 20. The same degree of susceptibility is present in tests conducted on pre-cracked specimens; however, the failure time is substantially less. Since fracture toughness generally decreases as yield strength increases and stress corrosion susceptibility, as measured by time to failure, is dependent for a given class of steels on fracture toughness, the general correlation between yield strength and failure time shown in Figure 20 should be expected. Considering that the tests used comparable environments, stresses, and specimens, it is significant to note that Figure 19 which represents data obtained in alternate immersion-drying tests, indicates failure times considerably less than those shown in Figure 20 where constant exposure was employed. The high nickel high-strength steels such as the HP 9-4 and 18% maraging steels are relatively resistant to stress corrosion failures. Figure 21 shows comparative data for the HP-9-4-45 and 4340 steels at a comparable yield strength level. The 9% nickel steel has considerably greater resistance to stress corrosion cracking however, the decreased stress range over which the stress corrosion failure occurs can be qualitatively related to the increased fracture toughness of the high nickel steels.

The relatively large number of tests that have been conducted on the stress corrosion susceptibility of steels has resulted in one significant conclusion. In the selection of high-strength steels for engineering applications, the materials with the greatest fracture toughness produce the greatest resistance to stress corrosion cracking and the greatest degree of overall reliability. Aside from this conclusion, which is related to mechanical behavior, no definite results relating alloy composition and stress corrosion are consistently evident.

6. METHODS FOR MINIMIZING STRESS CORROSION

In cases where stress corrosion exists, the effects can be minimized by introducing compressive residual stresses in the structure, by coating, or by polarization. Shot peening has been used effectively as a method of introducing surface-residual compressive stresses and thereby decreasing the effective tensile stress which is available to promote stress corrosion cracking²⁴. Methods of this type have been used on landing gears to decrease stress corrosion susceptibility.

A wide variety of coatings have been evaluated in bent beam tests conducted in a sea exposure²⁵. The types of coatings evaluated are listed in Table VII while test results are summarized in Table VIII. Aluminum applied after austenitizing prevented cracking in the steels evaluated. In addition, only one stressed specimen of eight,

coated with nickel-cadmium electroplate, failed in 263 days. Some of the coatings, such as the aluminum applied before austenitizing and the aluminum-pigmented silicone coating applied after austenitizing, were effective on some of the specimens. The results, however, were not consistent and relatively short term failures were also obtained with these coatings.

The electrode potential of uncoated steels was compared to the potential of the same steels in the coated condition to determine whether any correlation existed between the electrode potential of the coating and its ability to prevent stress corrosion. An aerated 3% NaCl solution was used as an electrolyte and all measurements were made with reference to a saturated calomel electrode. The coatings that were anodic to the bare steels were effective in preventing stress corrosion (zinc-dust dibutyl titanate primer, sprayed aluminum, and nickel cadmium electroplate) while those coatings that were cathodic provided no satisfactory protection.

In a second study involving 3% NaCl solutions and bent beam tests on H-11 and 18% nickel maraging steel, evaluations were conducted using three coatings-polyurethane, inorganic zinc, and inhibited epoxy¹⁰. The polyurethane represents a system where the coating merely acts as a dense barrier between base metal and environment, the inorganic zinc serves to provide cathodic protection for the base metal, while the inhibited epoxy coating protects the metal by both inhibitory action of the chromate compounds and the barrier effect.

Representative results obtained from these tests are shown in Table IX. In room temperature exposure, all the coatings showed some protective qualities with the inhibited epoxy system representing the most effective barrier and the inorganic zinc being the least effective. The same coatings were also tested at 140°F in air saturated with water. Once again the inhibited epoxy was the best protective system, while the inorganic zinc provide no protection whatsoever. There are also some indications that the protective qualities of the coatings may vary depending on the environment. Although certain coatings certainly show promise as preventative measures against stress corrosion, the reliability and overall effectiveness must be evaluated for each engineering situation.

Although cathodic protection is an effective method of reducing stress corrosion in stainless steel alloys, the method is not directly applicable to high-strength steels. Typical behavior obtained from polarization studies in environments of distilled water and 3% NaCl solution are shown in Figures 22 and 23 respectively. Using pre-cracked 300M high-strength steel specimens in distilled water, the failure times were substantially decreased by making the specimen cathodic. This effect results from a hydrogen embrittlement mechanism. In the case of bent beam specimens tested in the chloride environment, some cathodic protection was observed, however, the range was extremely narrow before the hydrogen embrittlement mechanism became operative. The use of cathodic protection is generally not considered as a practical method of reducing stress corrosion effects in high-strength steels.

7. CONCLUSIONS

High-strength steels are extremely susceptible to delayed failure in a variety of commonly encountered service environments. In engineering applications where strength-

to-weight ratios must be high, the tolerance of the material for stress corrosion induced cracks is low and this mode of failure represents a particularly critical design consideration.

From a laboratory evaluation standpoint smooth specimens, such as bent beam or U-bend provide a relative indication of stress corrosion susceptibility. Pre-crack specimens, however, have definite advantages since they can be used along with linear elastic fracture mechanics analysis, to provide a quantitative indication of the susceptibility of components with a known defect size. In addition, from a screening standpoint, the pre-cracked specimens produce failure in shorter times than the smooth specimens and provide results with a greater reproducibility.

Stress corrosion failures can be produced in high-strength steels exposed to distilled water environments at loads as low as one-half the normal strength in times of the order of hours. The addition of chlorides to the distilled water environment does not increase the stress corrosion susceptibility of the high-strength steels. Dry hydrogen and gaseous environments containing water vapor are also capable of producing stress corrosion effects in high-strength steels. In fact hydrogen has been found to promote crack propagation in high-strength steel at a faster rate than distilled water. In selecting materials for design purposes, the steels with the higher fracture toughness generally result in a greater resistance to stress corrosion failure. The 9% nickel quench and temper steels and the 18% nickel maraging steels have been found to possess the greatest resistance to stress corrosion in aqueous environments.

Although shot-peening and the application of coatings have minimized stress corrosion cracking, the results are often inconsistent and these possible solutions must be evaluated for each engineering application.

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APPENDIX A - Nominal Chemical Compositions of Steels Described in This Presentation (Weight %). See Page IV-39.

APPENDIX B - Illustration of Use of Fracture Toughness Parameter for Design Purposes. See Page IV-40.

TABLE I
Environments that Produce Stress Corrosion
Cracking in Carbon and Alloy Steels

<i>Medium</i>	<i>Type of Fracture*</i>	<i>Comments</i>
Aqueous chloride solutions	I, T	Particularly prevalent in high-strength steels.
Caustics	I	Well known as caustic embrittlement.
Nitrates	I	Examples exist of failures of bridge cable in ammonium nitrate or sodium nitrate environments.
HNO ₃	I	
HCN	T	
Sea coast and industrial atmosphere		High-strength steels (yield strength above 200 ksi) are particularly susceptible.
Water, humid gas, dry hydrogen		High-strength steels (yield strength above 200 ksi) are particularly susceptible.
Molten zinc	I	
H ₂ S	I, T	
H ₂ SO ₄ -HNO ₃	I	
H ₂ SO ₄	I	

* I - Indicates intergranular fracture; T - Indicates transgranular fracture.

TABLE II

Bent-Beam Stress-Corrosion Test Data, 3% Sodium Chloride Solution*
(Ref. 10)

Alloy	Yield Strength 0.2% Offset lb/in. ² × 10 ⁻³	No. of Specimens	Time to Failure (days)	Total Testing Time (days)
Ladish D6AC	198.0	3	NF†	21
	223.0	3	NF	21
	235.0	3	NF	21
	252.0	3	NF	21
Type 300M	196.0	3	NF	21
	213.0	3	NF	21
	233.0	3	NF	21
H-11	194.0	3	NF	21
	212.0	3	NF	21
	238.0	1	6.9	-
	238.0	1	10.0	-
	239.0	1	10.1	-
	242.0	1	1.2	-
	242.0	1	1.7	-
	242.0	1	6.7	-

* Stressed at 75% of the yield strength.

† No failure.

TABLE III

U-Bend Stress-Corrosion Test Data, 3% Sodium Chloride Solution
(Ref. 10).

Alloy	Yield Strength 0.2% Offset lb/in. ² × 10 ⁻³	No. of Specimens	Time to Failure (days)	Total Test Time (days)
Ladish D6AC	198.0	2	NF*	27
	223.0	2	NF	27
	235.0	2	NF	27
	252.0	1	18.5	-
Type 300M	196.0	2	NF	27
	213.0	1	NF	27
	213.0	1	11.3	-
	233.0	1	11.3	-
	233.0	1	26.3	-
H-11	194.0	2	NF	27
	212.0	1	NF	27
	212.0	1	13.7	-
	240.0	1	4.3	-
	240.0	1	6.8	-

* No failure.

TABLE IV
Test Techniques used to Measure Stress Intensity Factor (K)

Test Method	Conditions for Accurate Measurement of K_{IC}	Method of Calculating* K
Tensile test on pre-cracked round specimen	$\sigma_N < 1.1 F_{TY}$	$K = 0.414 \sigma_N \sqrt{D}$ (formula applies for notch specimens where $d/D = 0.707$)
Tensile test on center notch, pre cracked sheet specimen	$\sigma < 0.8 F_{TY}$ $n_p < \frac{1}{10} B$	$K_C = \sigma \left[W \tan \frac{\pi a_0}{W} \right]^{1/2}$
Tensile test on surface-cracked specimen	$\sigma_f < F_{TY}$	$K_{IC}^2 = \frac{3.77 \sigma^2 b}{\phi^2 - 0.212 \left(\frac{\sigma}{F_{TY}} \right)^2}$
Single notch specimen	$0.2 < (a_0/W) < 0.5$ $\sigma_f < F_{TY}$	$K = \frac{P^2}{B^2} \frac{1}{W} \left[7.59 \frac{a_0}{W} - 32 \left(\frac{a_0}{W} \right)^2 + 117 \left(\frac{a_0}{W} \right)^3 \right]$
Bend test	$\sigma_f < F_{TY}$ $0.2 < a_0/W < 0.5$	$K = \frac{P^2 L^2}{B^2 W^3} \left[31.7 \left(\frac{a_0}{W} \right) - 64.8 \left(\frac{a_0}{W} \right)^2 + 211 \left(\frac{a_0}{W} \right)^3 \right]$ (3 point loading)
<p>* All K values are corrected for plasticity by adding a plastic zone size $r_p = \frac{K^2}{6\pi\sigma_y^2}$ to the crack length a_0.</p> <p>σ_N - net notch tensile strength W = specimen width $2a_0$ = initial crack size in center notch specimen a_0 = crack size in bend and single edge notch specimens σ = gross stress at start of crack growth F_{TY} = 0.2% yield strength</p> <p>b = crack depth in surface crack specimen a = crack length in surface crack specimen $b = \text{elliptic integral} \left(\phi^2 = \int_0^{\pi/2} \sqrt{1 - \left(\frac{a^2 - b^2}{a^2} \right) \sin^2 \theta} d\theta \right)$ b = thickness L = distance between load and support plus P = applied load</p>		

TABLE V

Comparison of Stress Corrosion Test Duration Using Bent Beam
Specimen Without a Pre-Crack and Pre-Cracked Tensile Specimens,
4340 Steel, Distilled Water Environment

<i>Specimen Type</i>	<i>Material Yield Strength (ksi)</i>	<i>Applied Stress (ksi)</i>	<i>Failure Time (hours)</i>
Bent beam	220	176	1000
Bent beam	220	176	No failure in 4500
Bent beam	225	180	No failure in 2000
Bent beam	240	192	700
Center pre-cracked tensile	213	40	0.17
Center pre-cracked tensile	213	40	0.13
Center pre-cracked tensile	208	40	0.08
Center pre-cracked tensile	185	60	82

TABLE VI

Influence of Various Crack Environments on the Failure
Time of 300M Steel, Pre-Cracked Specimens Loaded
to 83% of the Notched Tensile Strength in Air

<i>Environment</i>	<i>Failure Time (min.)</i>
Recording ink	0.5
Distilled water	6.5
Amyl alcohol	35.8
Butyl alcohol	28.0
Butyl acetate	18.0
Acetone	120
Lubricating oil	150
Carbon tetrachloride	No failure in 1280
Benzene	2247
Air	No failure in 6000

TABLE VII
Coatings Tested
(Ref. 25)

Coating	Description	Measured Average Thickness (in.)
Ni-Cd electroplate	Specification AMS 2416; electroplated Ni 0.002 to 0.0004 in., followed by electroplated Cd 0.0001 to 0.0002 in., followed by diffusion at 630°F for 1 hr.	0.0005
Electroless Ni	Coated to 0.002-in. thickness, followed by postbaking heat-treatment.	0.0017
Electroplated Ni	"Gray Nickel" plate	0.0025*
Chromium	Commercial electroplating	0.0013
Aluminum	Al-metallizing, followed by dip coating with hydrolyzed ethyl silicate.	0.0057
Al-pigmented silicone	Baked 2 hr. at 425°F	0.0013
Silicone	Baked 2 hr. at 425°F	0.0005
Zinc chromate iron oxide alkyd paint	Primed and painted, air-dried	0.0019
Zinc chromate primer	Air-dried	0.0009
Zinc-dust dibutyl titanate	An experimental zinc-dust dibutyl titanate primer, air-dried	0.0021
Rust-preventive wax	Coating was applied to stressed specimens immediately before exposure	0.0012
Rust-preventive grease	Coating was applied to stressed specimens immediately before exposure	Not measured
Strontium chromate aluminum paint	Air-dried	0.0008
Aircraft-type zinc chromate primer	Specification MIL-P-6889A Type I, air-dried.	0.0002

* Coating peeled off during stressing on some specimens. These specimens were excluded from the test.

TABLE VIII

Effect of Protective Coatings on Stress Corrosion of Aircraft Alloys*
(Ref. 25)

Coating	Time to Failure (days)	
	12 MoV	Die Steel
Not Coating	0.7	1.5 to 3
Coatings that prevented stress corrosion		
Alumin... applied after austenitizing	NF	NF
Coatings that delayed stress corrosion		
Ni-Cd electroplate	NF	263**
Zinc-dust dibutyl titanate	NF	395**
Aluminum applied before austenitizing	4 to 66	46**
Al-pigmented silicone applied after austenitizing	7**	147**
Aircraft-type zinc chromate primer	2 to 17	-
Electroplated Ni	405**	0.7
Coatings with no appreciable effect on stress corrosion		
Electroless Ni	0.7	0.7 to 1
Electroplated Cr	0.7	0.01 to 4
Al-pigmented silicone applied before austenitizing	0.7	2 to 3
Silicone	0.7	0.7 to 5
Zinc chromate iron oxide alkyd paint	0.7 to 3	0.7 to 13
Zinc chromate primer	0.7 to 1	-
Rust-preventive wax	0.7 to 13	0.7 to 4
Rust-preventive grease	0.7 to 3	0.7 to 5
Strontium chromate aluminum paint	0.7 to 1	-

NF = No failure in 420 days.

* Results of exposure at Kure Beach, N.C.

** Some specimens have not failed after 420 days.

TABLE IX
Bent-beam Stress-Corrosion Tests for Coatings Evaluation
(Ref. 10)

Base Metal	Coating	3% NaCl Solution		140°F Water-Sat. Air	
		Failure Ratio*	Median Failure Time (hours)	Failure Ratio*	Median Failure Time (hours)
H-11 steel	None	4/4	1.5	2/2	64
H-11 steel	Polyurethane X-500	3/3	1380	6/6	3500
H-11 steel	Inorganic zinc - 11	2/2	687	2/2	821
H-11 steel	Inhibited epoxy 454-1-1	0/2	NF 3100	3/3	2720
18%-nickel maraging steel	None	3/3	119	3/3	535
18%-nickel maraging steel	Polyurethane X-500	1/3	4488	3/3	1560
18%-nickel maraging steel	Inorganic zinc - 11	3/3	288	3/3	140
18%-nickel maraging steel	Inhibited epoxy 454-1-1	0/3	NF 4990	2/3	1870

* Ratio of samples failed to samples exposed.

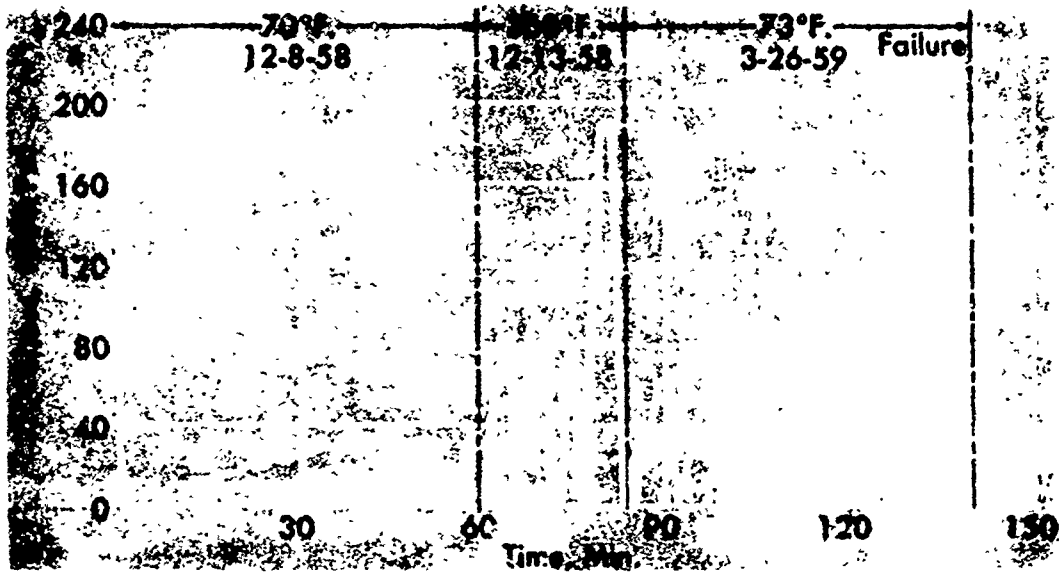


Fig.1 Testing schedule of full-size pressure vessel which failed (Ref.3)*



Fig.2 Inner surface of full-scale missile casing after fracture. Arrow points to origin of failure (Ref.3)

Note: In the Figures, psi denotes lb/in.²,
ksi denotes kips/in.² = 1000 lb/in.²

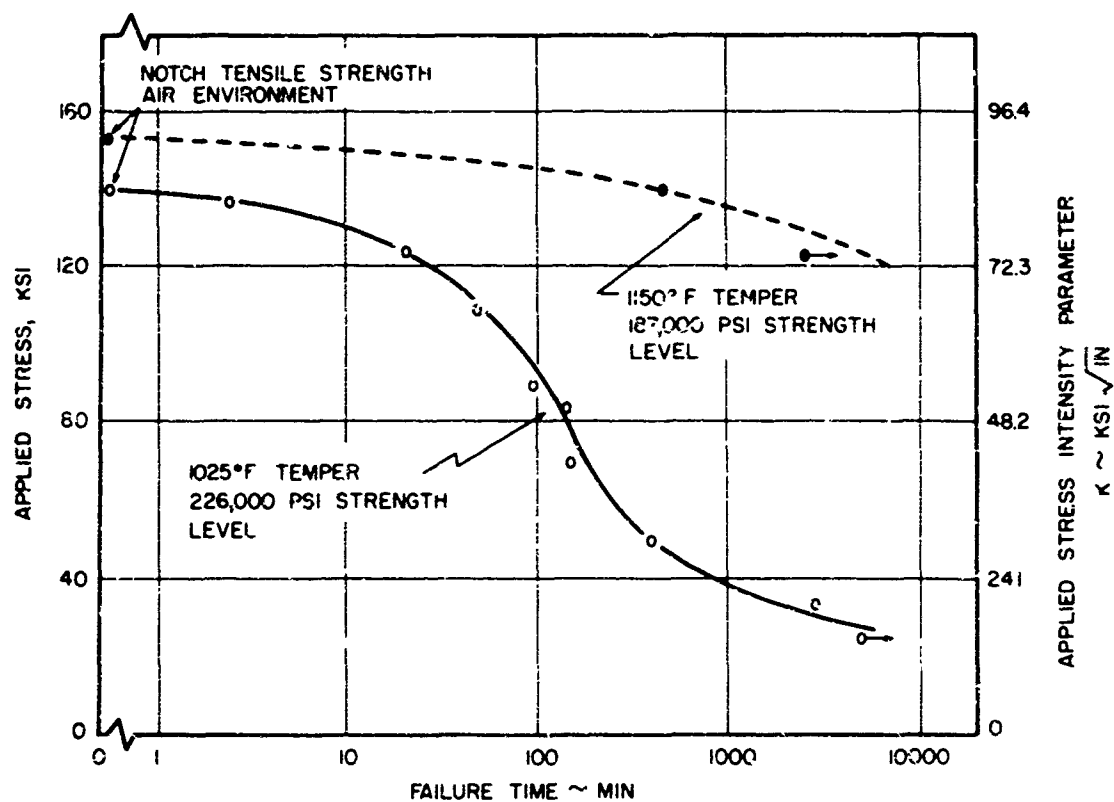


Fig.3 Delayed failure of 300M steel center pre-cracked specimens subjected to a distilled water environment (Ref.6)

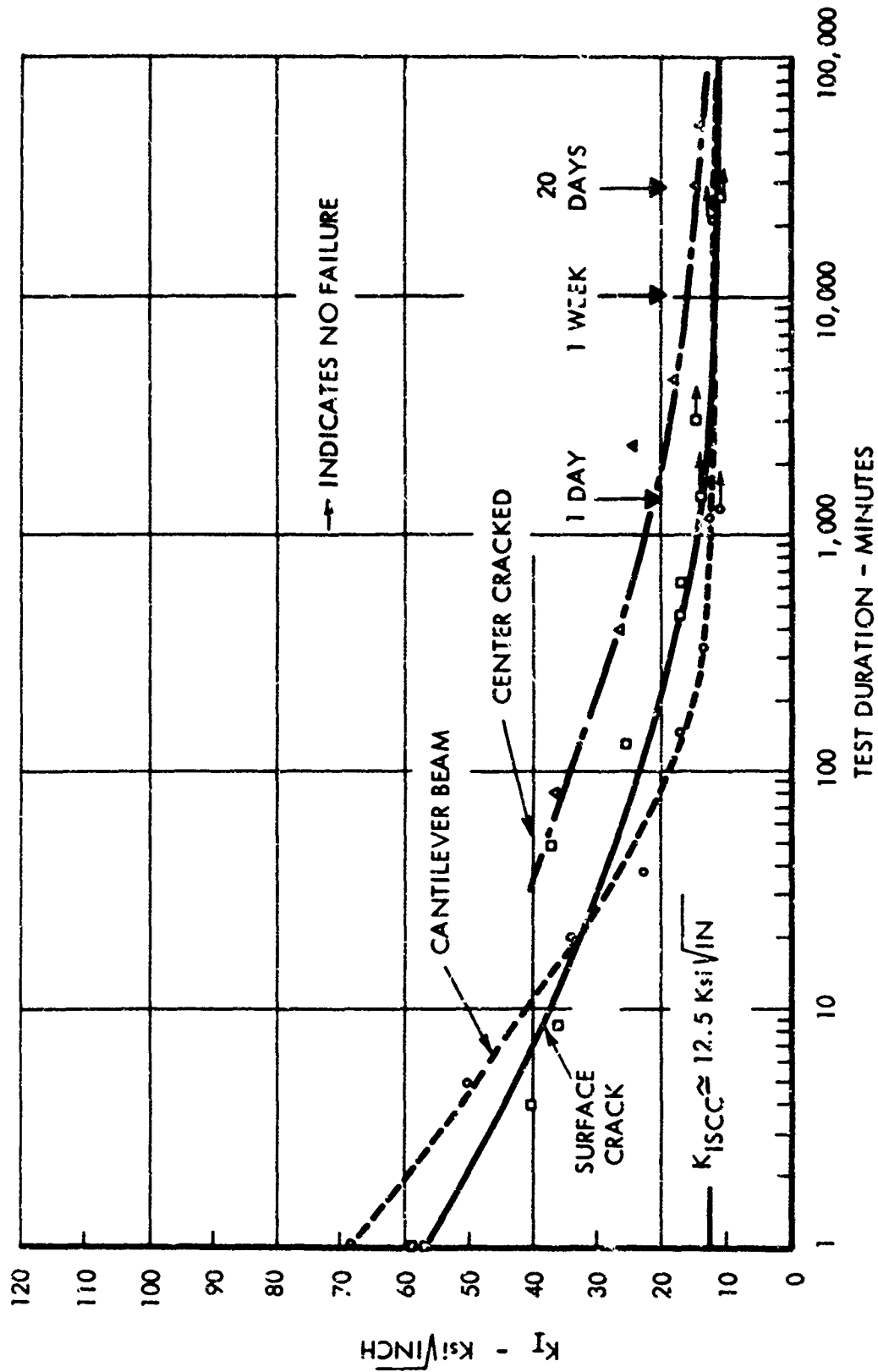


Fig. 4 Stress-corrosion cracking tests of AISI 4340 steel, using various-cracked specimens in 3½ percent NaCl solution (Ref. 15)

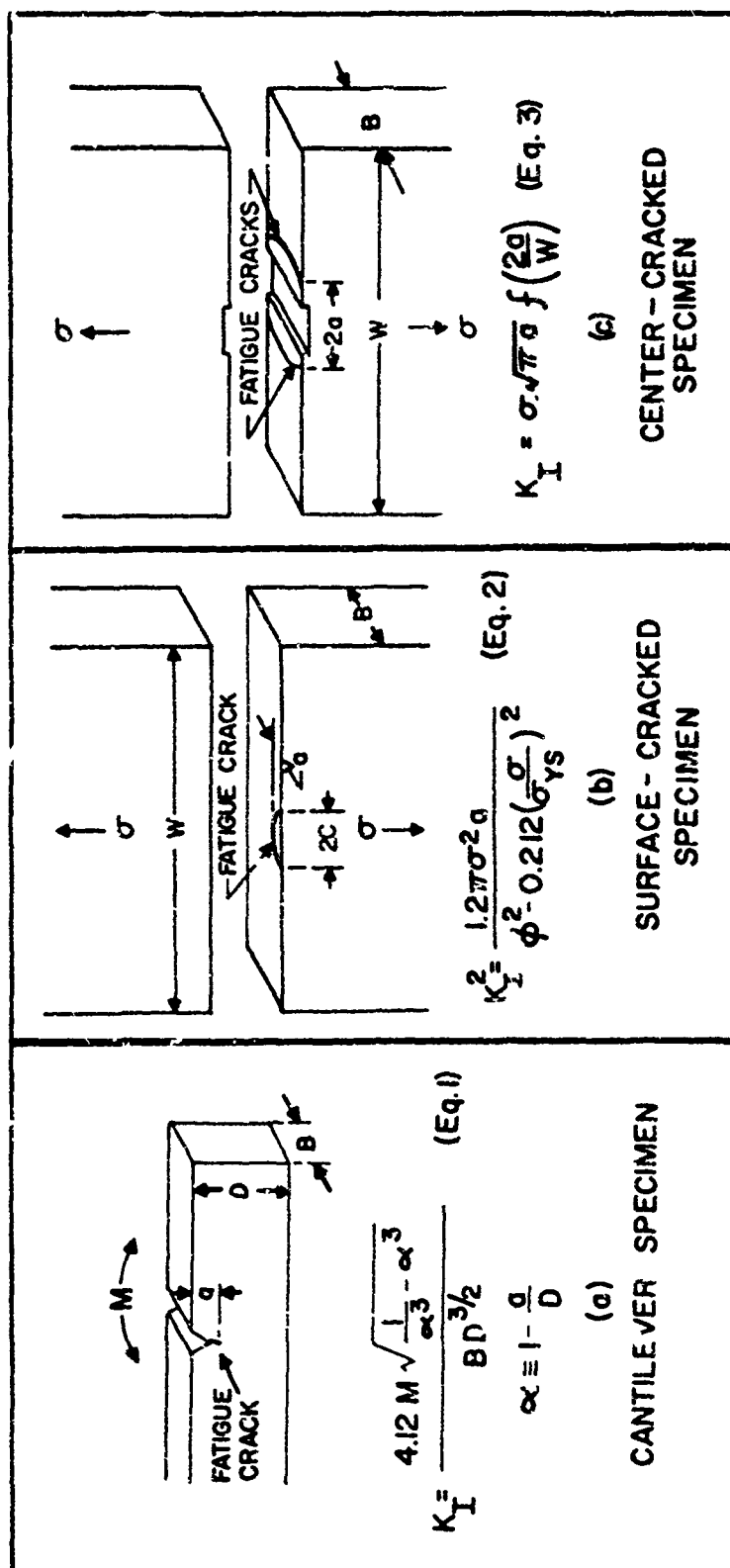
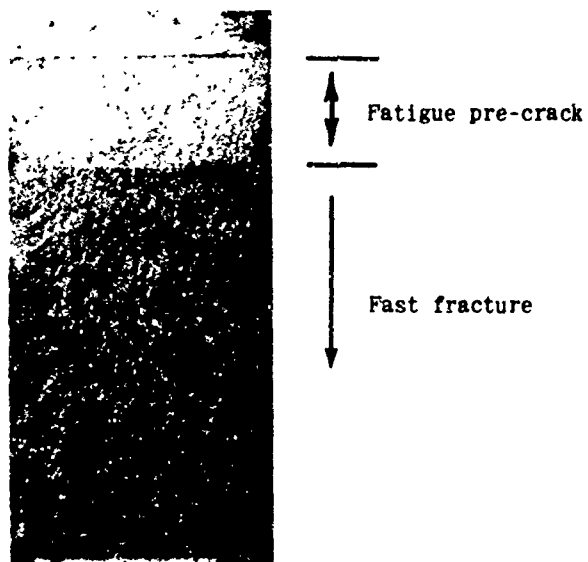
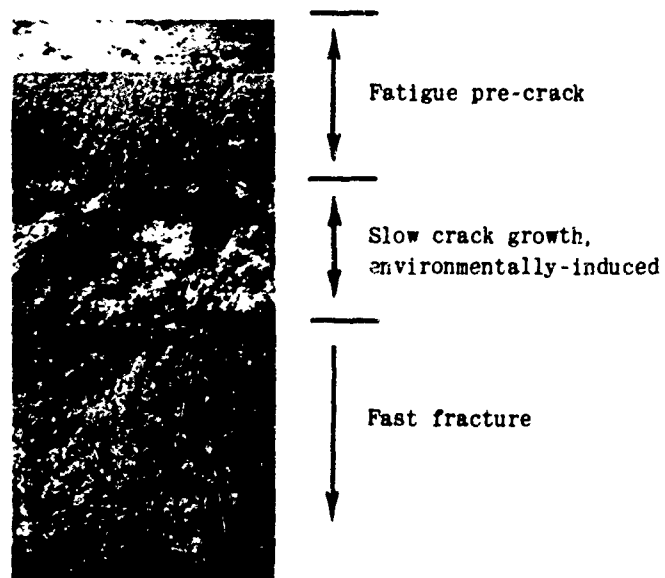


Fig. 5 Specimen dimension identification and equations. (a) cantilever-beam specimen, (b) surface-cracked specimen, (c) center-cracked specimen (Ref. 15)



Air environment
 $K_{IC} = 73.3 \text{ ksi in.}$



Distilled water
 Environment
 $K_I = 62.2 \text{ ksi in.}$

Fig.6 Fracture appearance of 4340 cantilever beam bend specimens, 235 ksi strength level

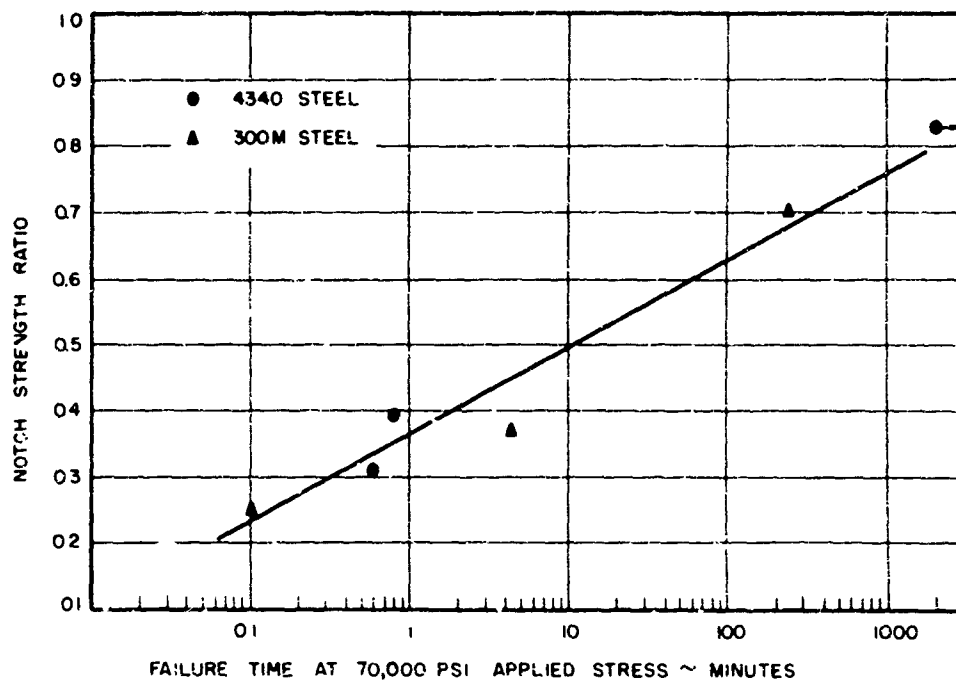


Fig.7 Relationship between notch strength ratio and failure time for the low alloy martensitic high-strength steels (Ref. 16)

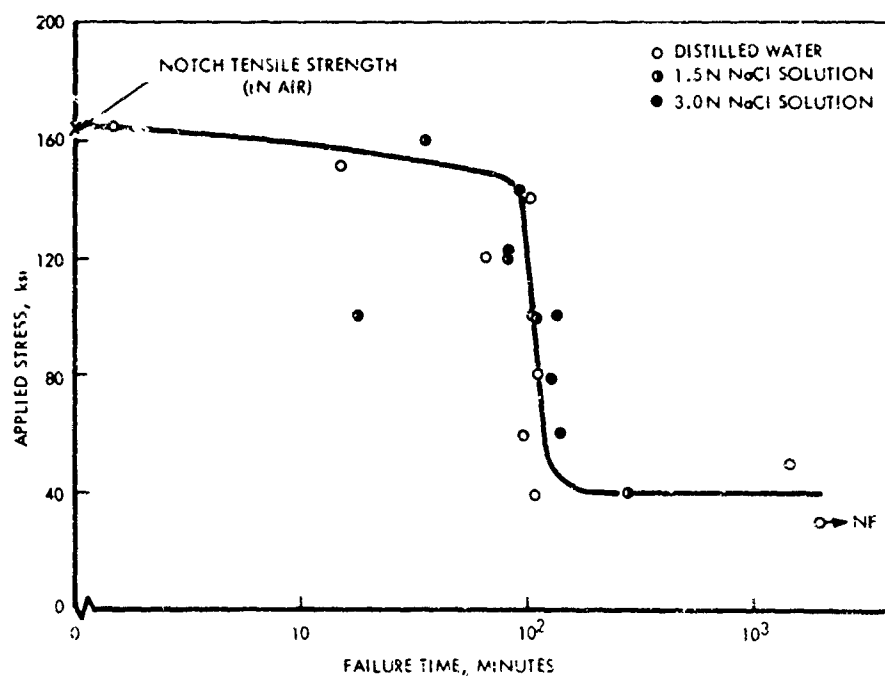


Fig.8 Delayed failure of AISI 4340 steel (235 ksi strength level) 0.050 in. sheet at 70°F (Ref. 18)

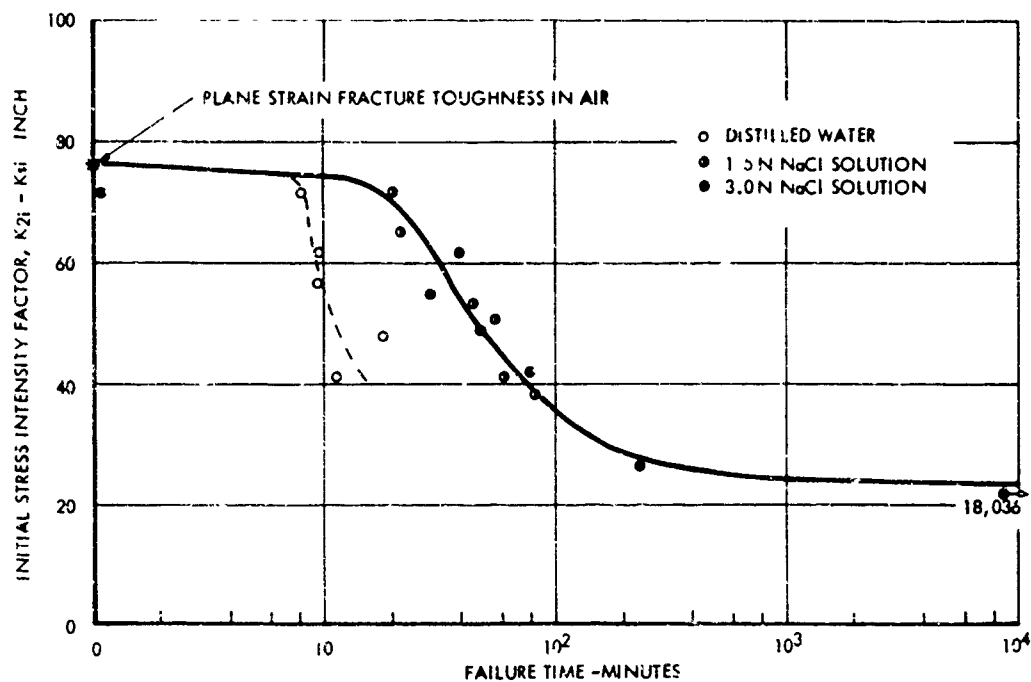


Fig.9 Influence of NaCl content on delayed failure time of AISI 4340 steel in aqueous solutions (cantilever loaded notch bend specimens) (Ref.18)

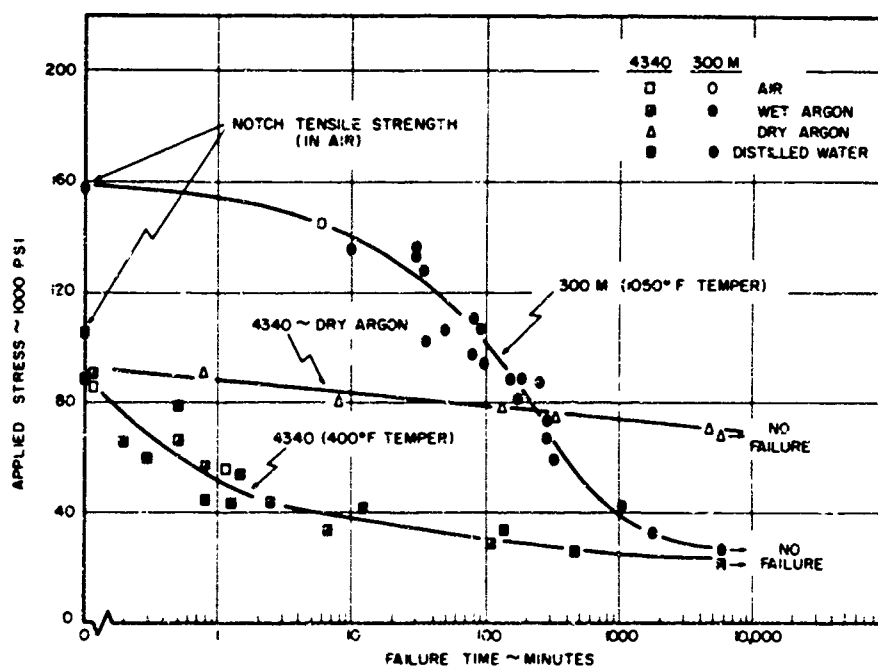


Fig.10 Comparison of air, argon and distilled water environments on delayed failure characteristics of 4340 and 300M steels at 68°F

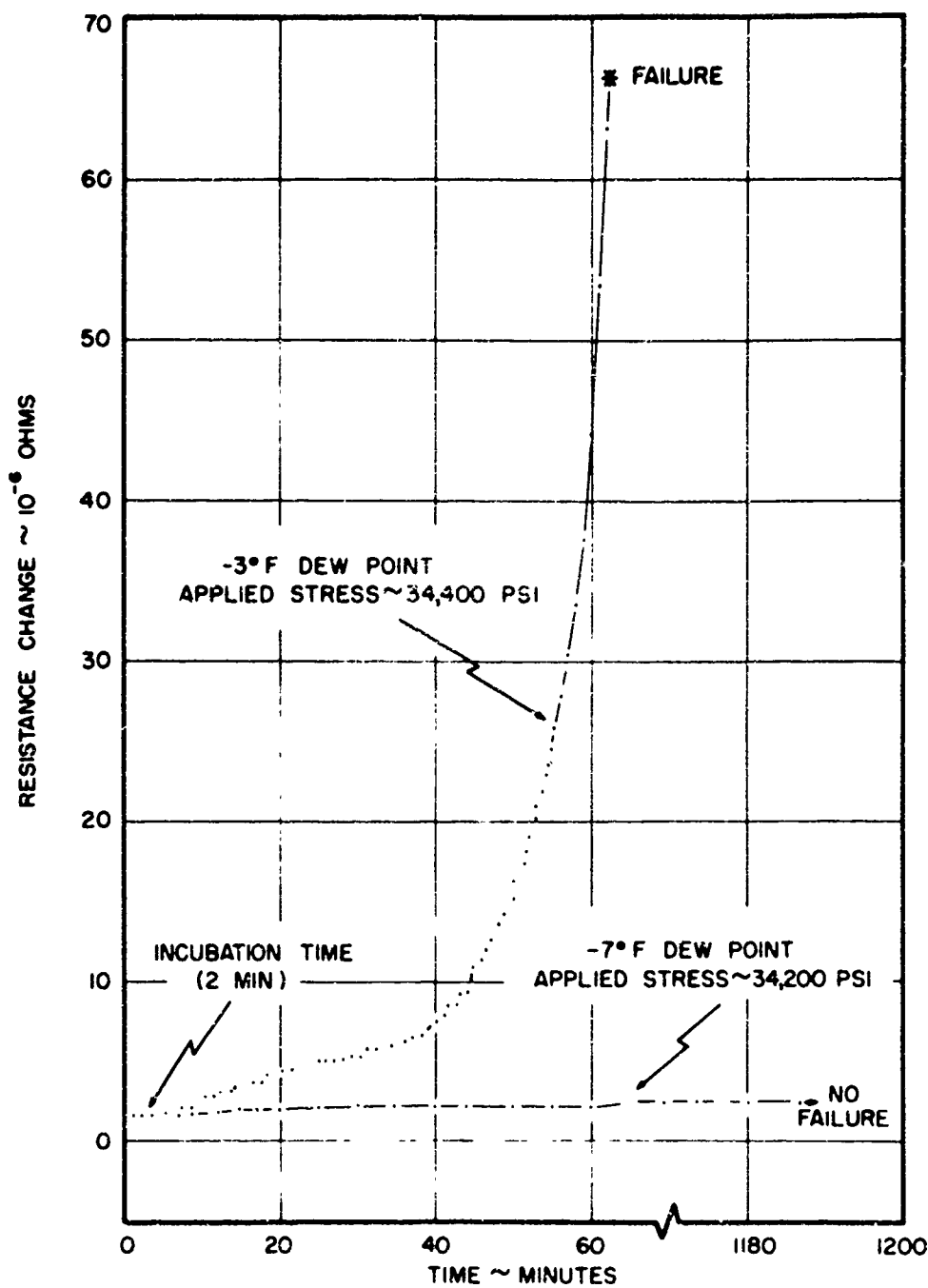


Fig.11 Effect of dew point on susceptibility of 4340 steel, 400°F temper, to cracking in argon environments at 68°F

IV-30

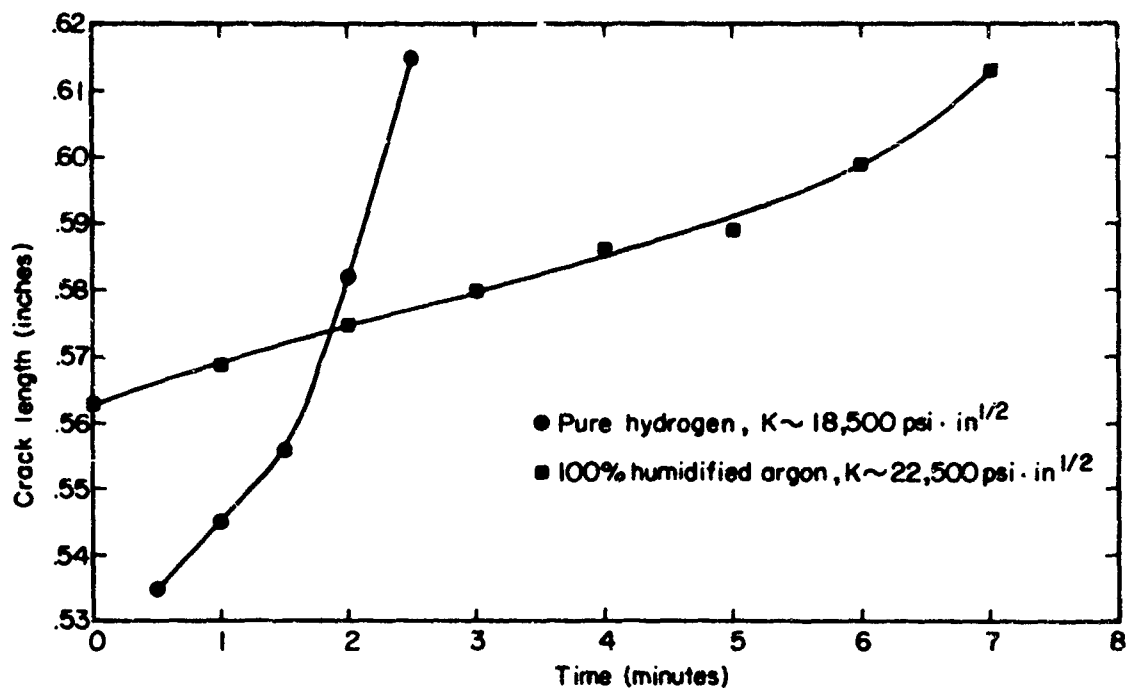


Fig.12 Subcritical crack-growth kinetics in hydrogen and humidified argon, H-11 steel (Ref. 20)

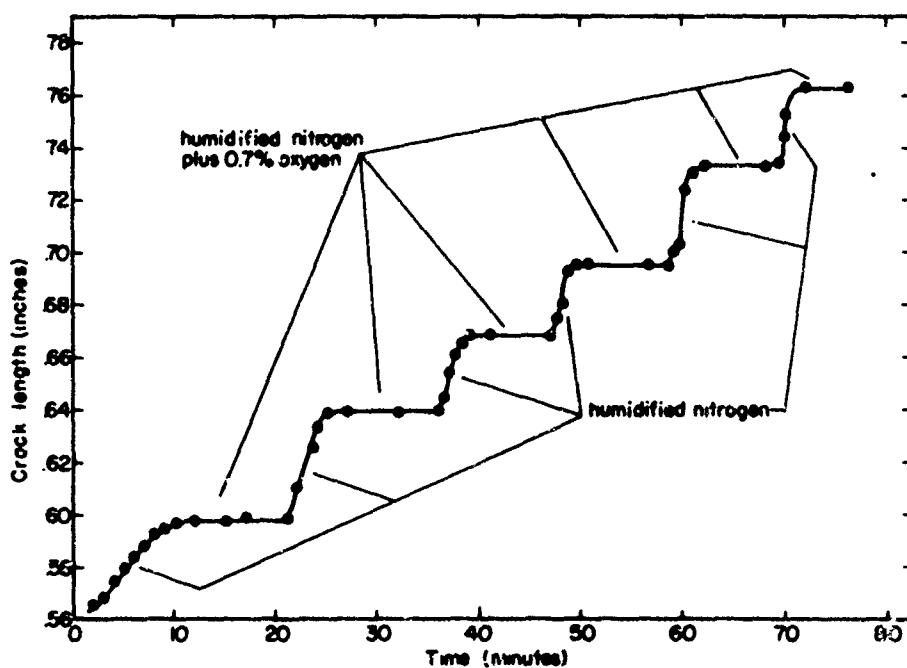


Fig. 13 Effect of 0.7% O_2 upon subcritical crack-growth in humidified nitrogen, H-11 steel (Ref. 20)

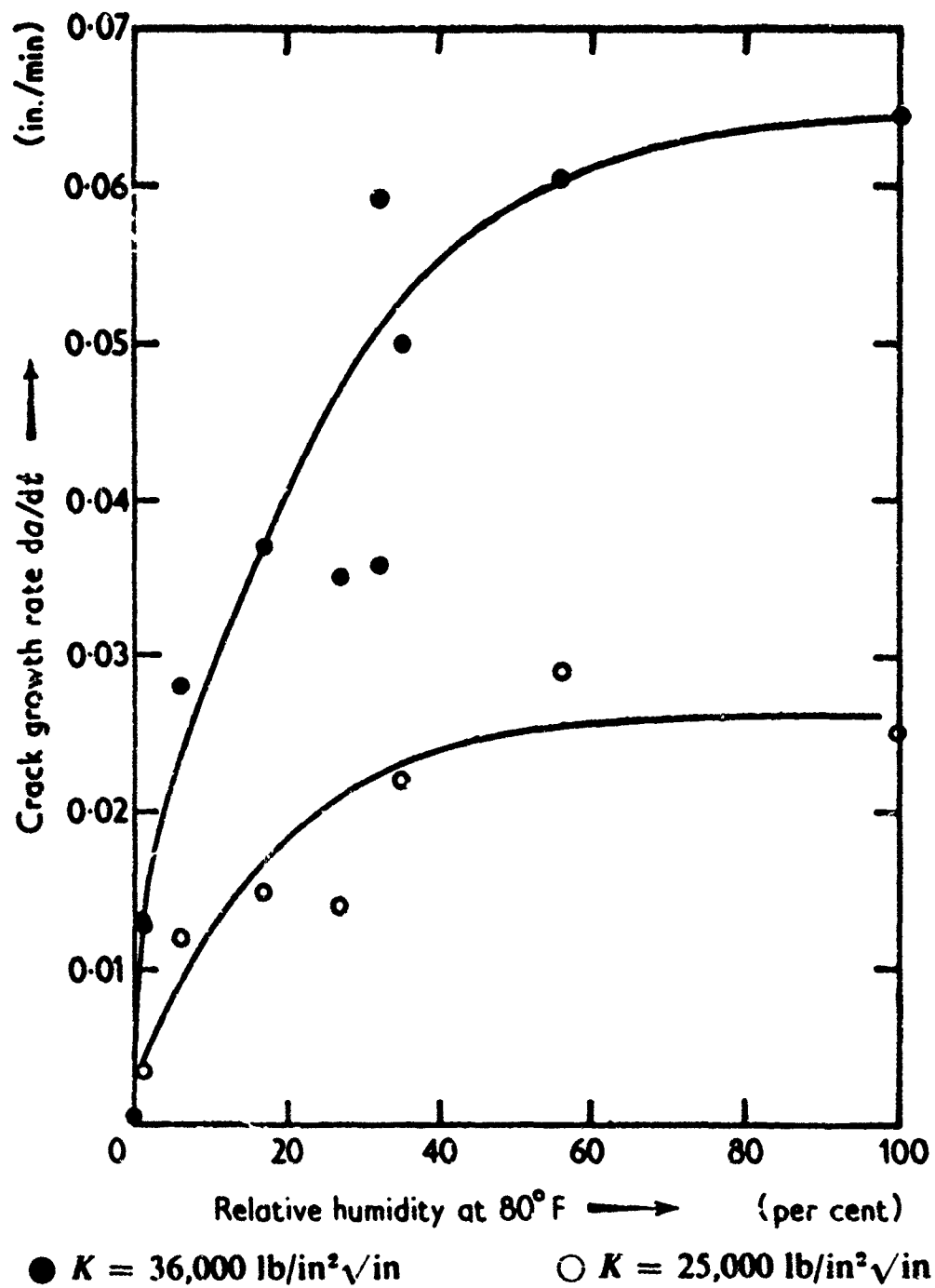


Fig.14 Crack-growth rate versus relative humidity, H-11 steel (Ref.21)

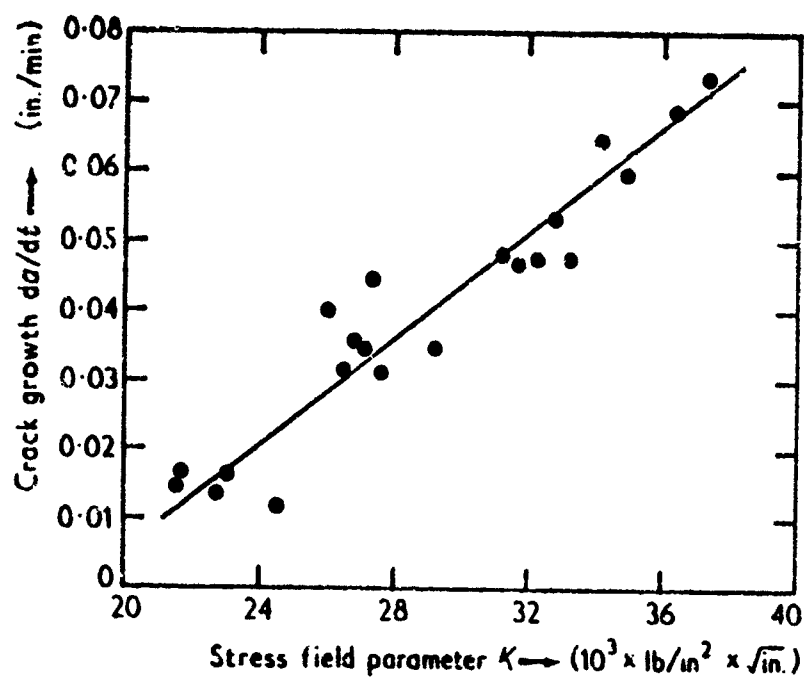


Fig. 15 Crack-growth rate versus field parameter for 100% relative humidity at 80°F. Data for H-11 steel, at 230,000 lb/in.² yield strength

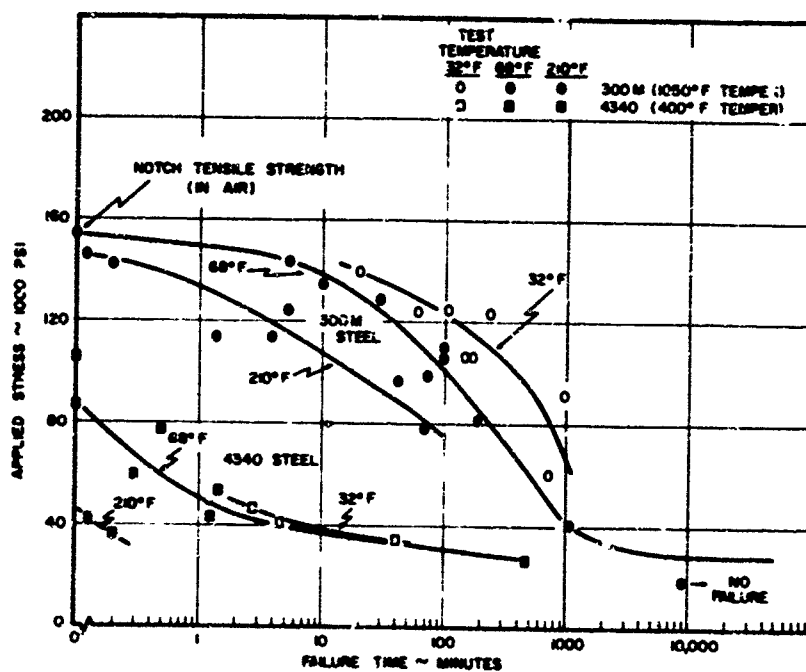


Fig. 16 Effect of temperature on delayed failure characteristics of 4340 and 300M steels in distilled water

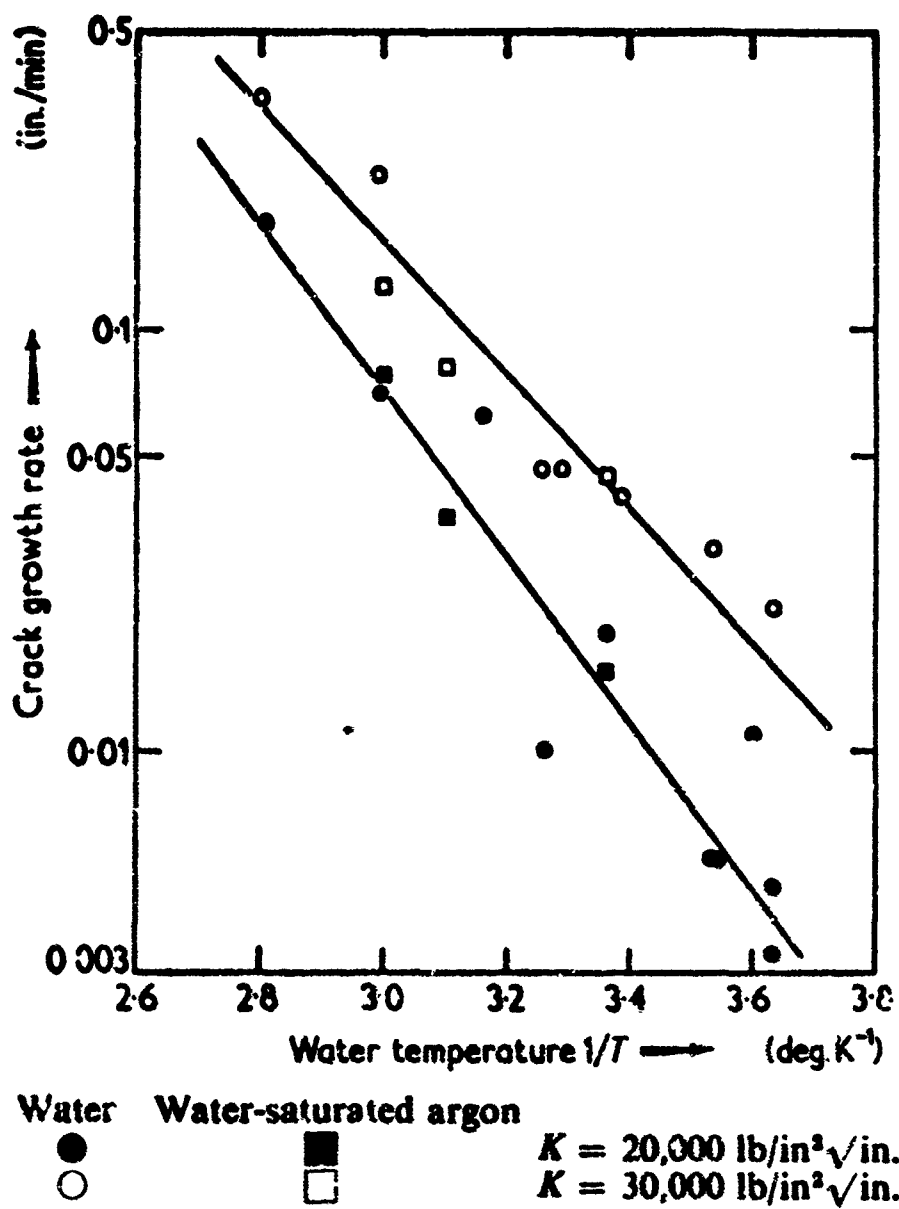


Fig. 17 Crack growth rate as a function of water temperature. H-11 steel activation energy approximately 9000 cal/mole (Ref. 21)

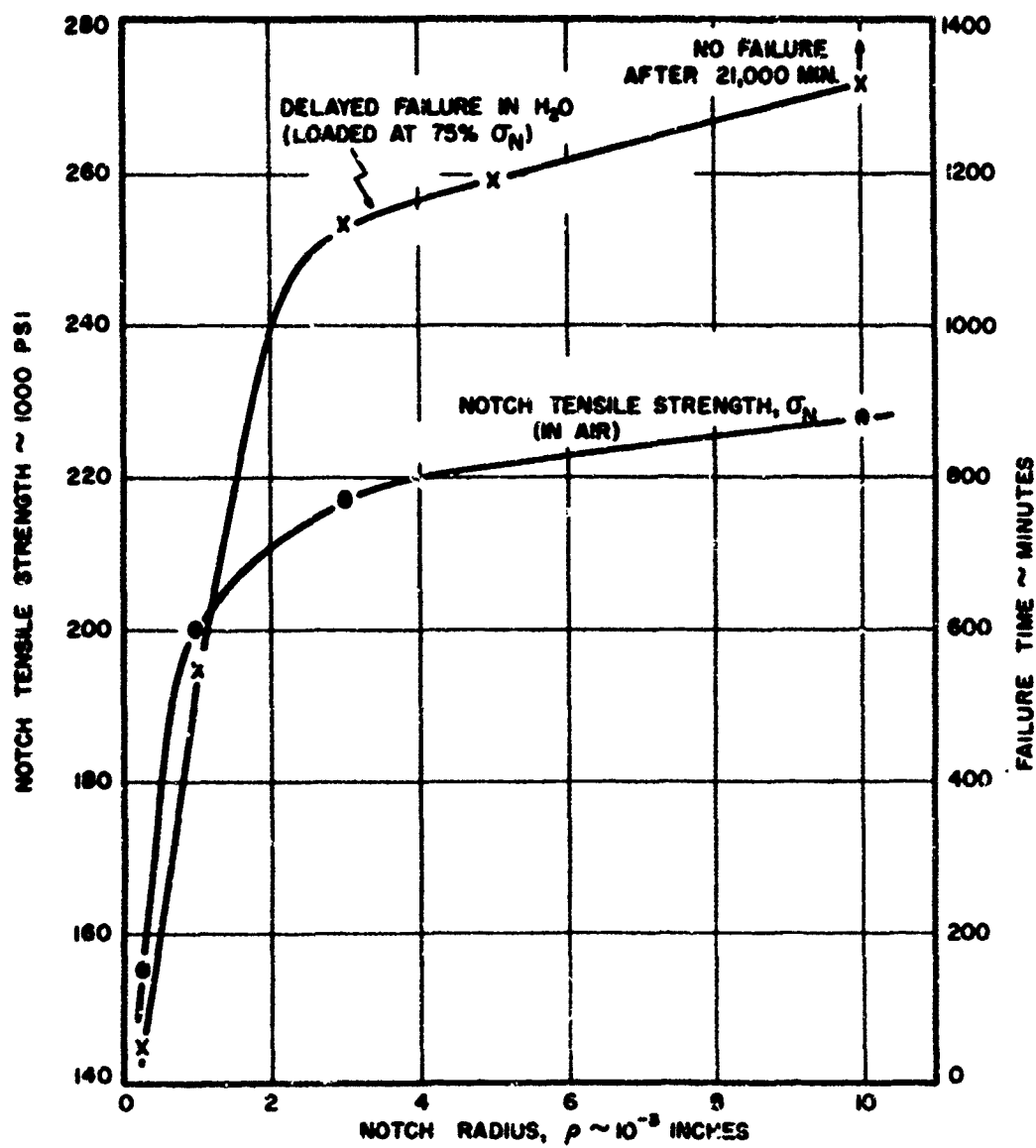


Fig.18 Effect of notch radius on notch tensile strength and delayed failure characteristics of 300M steel, 1050°F temper, at 68°F

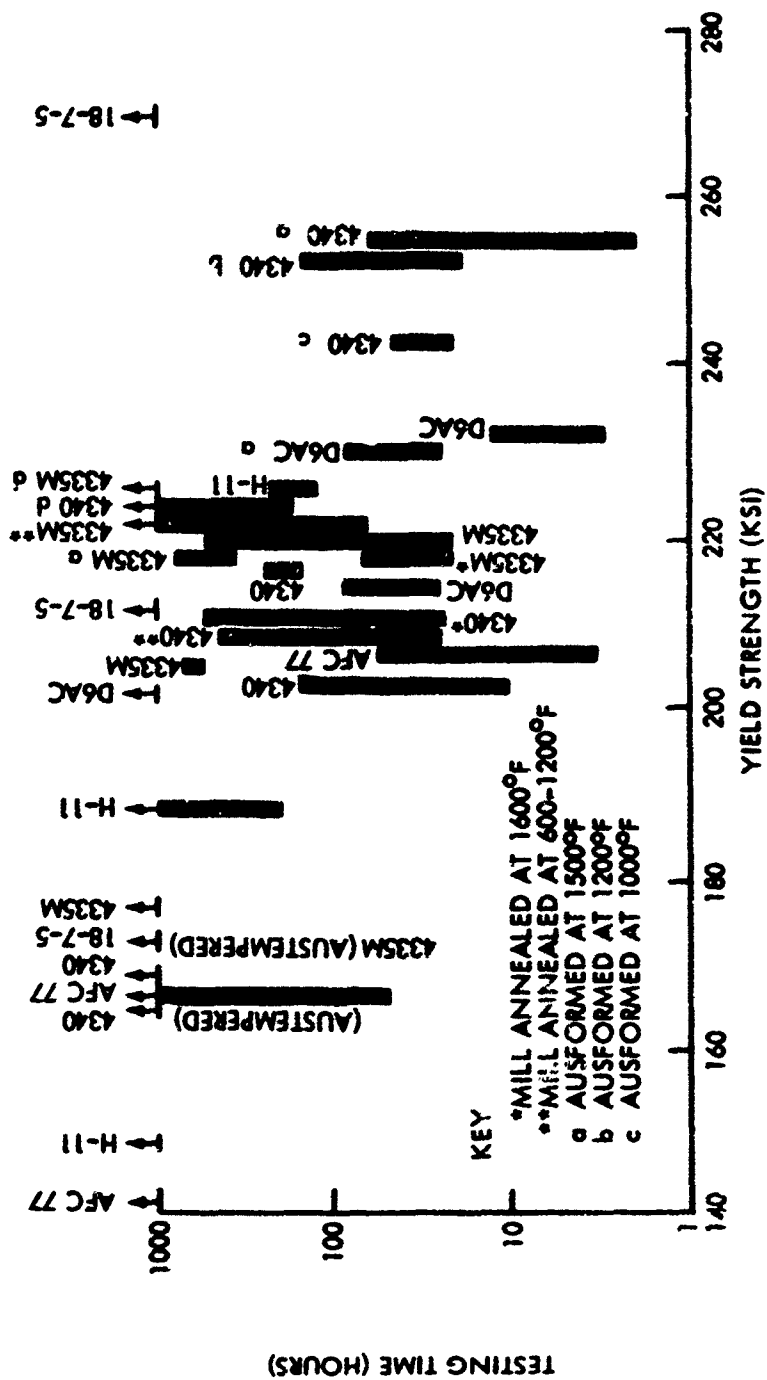


Fig. 19 Relative stress corrosion susceptibility of billet materials. All steels stressed to 80% of yield alternate immersion tests (Ref. 23)

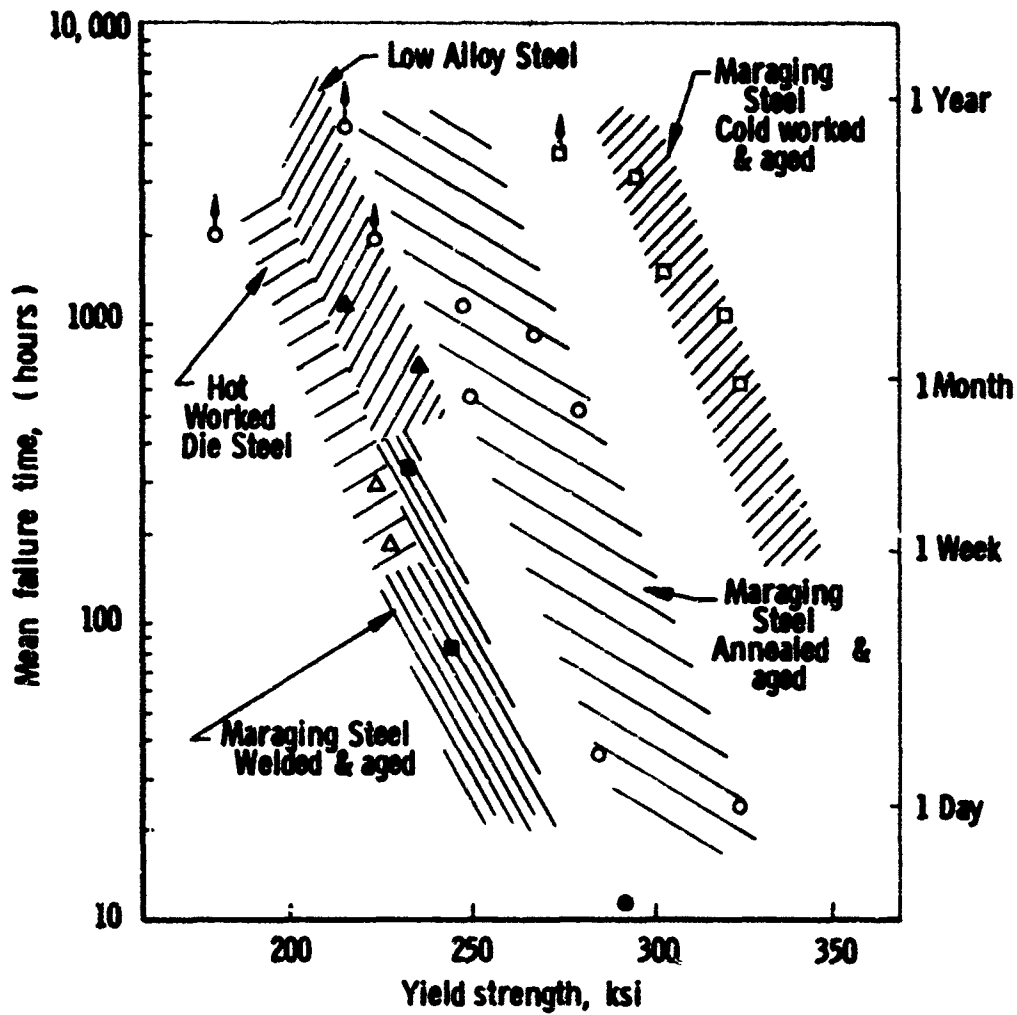


Fig. 20 Aerated distilled water, bent beam tests (Ref.10)

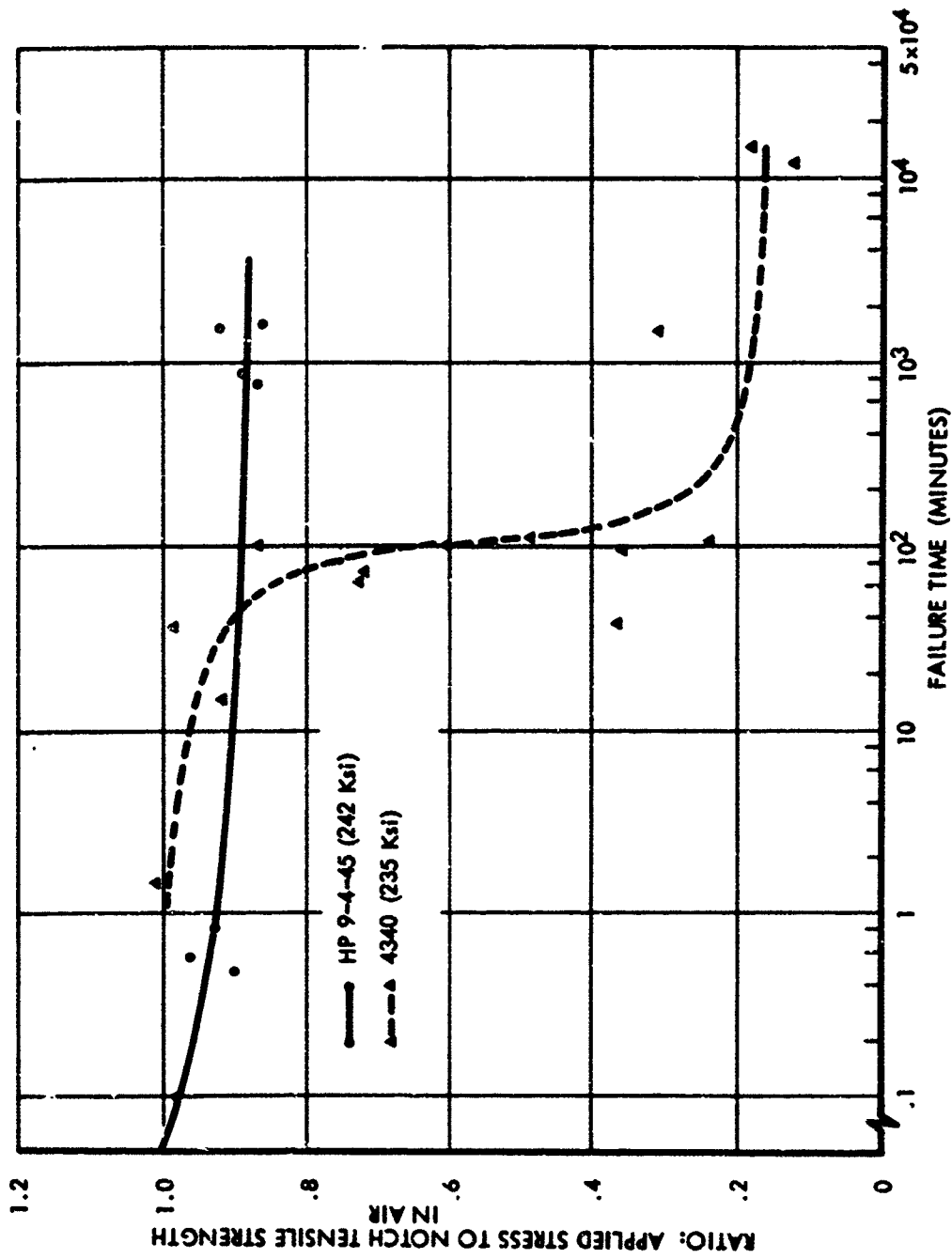


Fig. 21 Delayed failure of HP 9-4-45 center-notched pre-cracked specimens compared with 4340 steel, distilled water environment

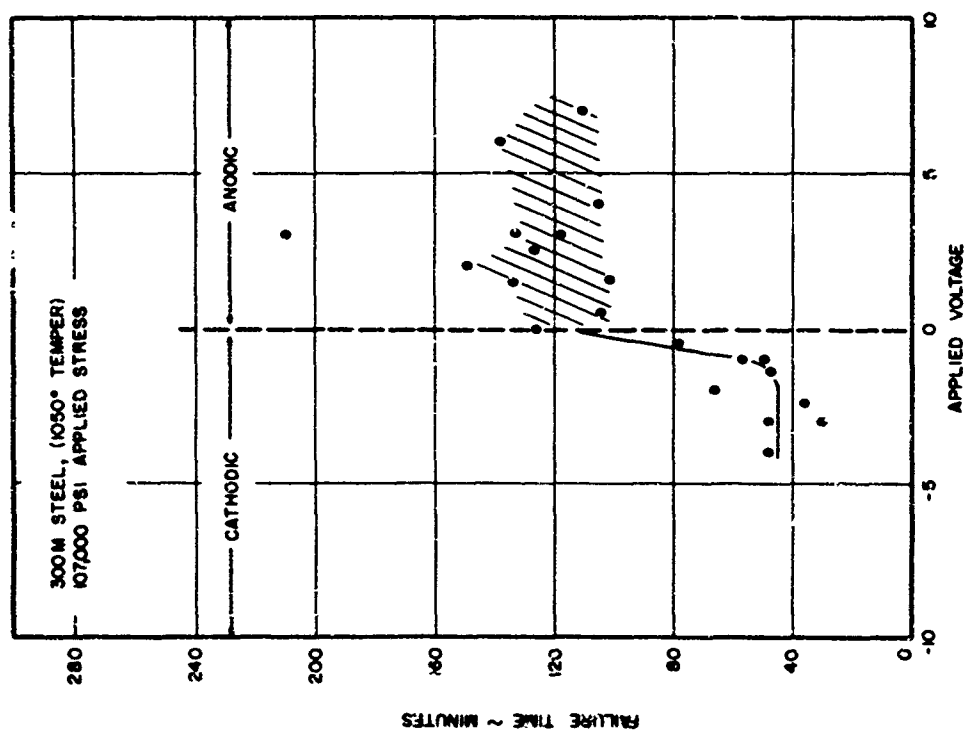


Fig. 22 Effect of applied electrical potentials on failure time of 300M steel in distilled water at 68°F (Ref. 16)

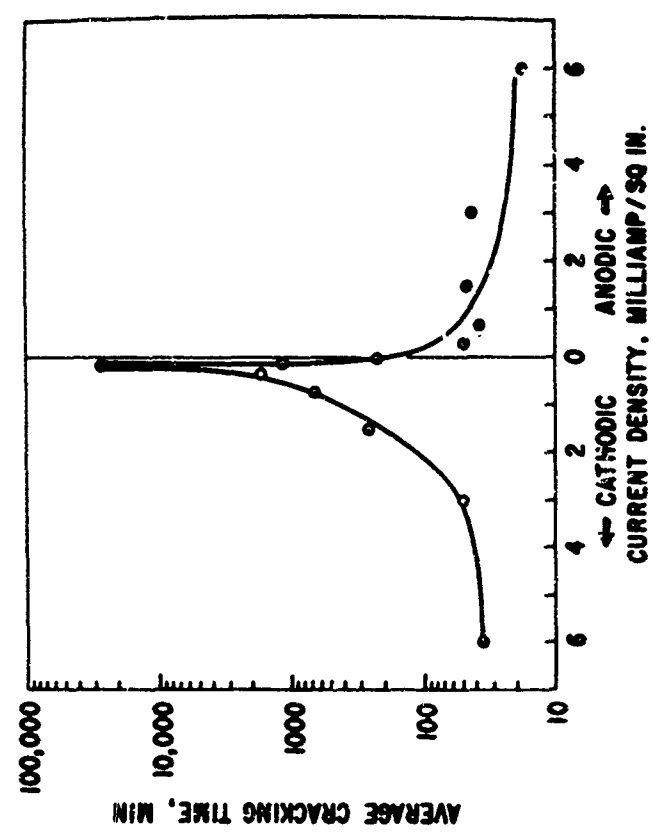


Fig. 23 Effect of applied current on cracking time, USS 12 MoV stainless steel in aerated 3% NaCl solution (Ref. 25)

APPENDIX A

**Nominal Chemical Compositions of Steels
Described in this Presentation (Weight %)**

<i>Steel</i>	C	Mn	Si	Ni	Cr	Mo	V	P	S	Fe	Co
H-11	0.42	0.29	0.96	-	5.17	1.35	0.52	0.021	0.006	Bal	
4340	0.40	-	-	1.85	0.90	0.40	-	-	-	Bal	
300M	0.40	-	1.75	1.85	0.90	0.40	-	-	-	Bal	
18% Ni Maraging (18-7-5)	0.007	0.03	0.01	18.0	-	4.82	-	-	-	Bal	7.45 0.39 Ti. 0.10 Al
HP 9-4-45	0.43	0.15	0.01	7.80	0.32	0.30	0.09	0.006	0.009	Bal	3.95
D6AC	0.45	0.69	0.26	0.55	1.0	1.0	0.08	0.008	0.006	Bal	
4335	0.35	-	-	1.85	0.90	0.40	0.52	-	-	Bal	
12 MoV	0.25	0.50	0.45	0.63	12.16	0.98	0.33	0.019	0.015	Bal	

APPENDIX B

Illustration of Use of Fracture Toughness
Parameter for Design Purposes

The use of the fracture mechanics concepts for design purposes will be illustrated by presenting several examples which characterize applications in material selection and post failure analysis.

Example i

The first example will involve a pressure vessel made from H-11 steel. The properties of the H-11 material as obtained from MIL Handbook 5 are presented in Table B-1 along with the K_{IC} parameters obtained from tests on sheet specimens.

For the basis of this illustration, consider the flaw as a partial surface crack and assume that the nondestructive testing technique is capable of detecting cracks greater than 0.050 in. in depth. This implies that cracks 0.050 in. or less may be present in the completed structure. For a partial surface crack, the plane strain toughness can be expressed as

$$K_{IC}^2 = \frac{3.77 \sigma^2 b}{\phi^2 - 0.212 \sigma^2 / \sigma_{ys}^2}$$

where K_{IC} is the plane strain fracture toughness,

σ is the gross applied stress,

$2a$ is length of surface crack,

b is depth of surface crack,

σ_{ys} is 0.2% yield strength,

ϕ is an elliptic integral defined as

$$\phi^2 = \int_0^{\pi/2} \sqrt{1 - \frac{(a^2 - b^2)}{a^2} \sin^2 \theta} d\theta.$$

For reliable performance the vessel should be capable of sustaining an applied stress (σ) which is equal to the yield strength (σ_{ys}). For the H-11 steel with a 220,000 lb/in.² yield strength and a crack length to depth ratio of 2, the calculations indicate that the K_{IC} value should be greater than approximately 64,000 lb/in.² $\sqrt{(\text{in.})}$ to insure that the defect does not grow and lead to failure below the design stress. Since the actual K_{IC} value for this strength level in the 5Cr-40-V steel is 41,000 lb/in.² $\sqrt{(\text{in.})}$, the designer would select a material with a higher fracture toughness or decrease the applied stress level. This quantitative approach to predicting the stresses where flaws start to grow as cracks can be applied to virtually any component provided that adequate stress analyses are available to define the relationship between the material constant K_{IC} and the crack geometry.

Example 2

A very promising area where fracture mechanics can be used in design is in the prediction of time-dependent failures (stress corrosion or fatigue). Taking fatigue as an example, conventional fatigue data are generally obtained on small laboratory samples and plotted as an S-N curve. The problem from a design standpoint is that the absolute value of the stress required to produce a given number of cycles to failure is dependent on the specimen geometry, just as in the case of notch tensile properties. However, if the fatigue curve is expressed in terms of the stress intensity parameter, a basic curve is then obtained which is independent of geometry. The fracture mechanics approach has been used by Tiffany to predict low cycle fatigue behavior in pressure vessels*. The fatigue results obtained on pre-cracked laboratory specimens are shown in Figure B-1. The results are presented as the ratio of applied stress intensity factor to the fracture toughness (K_I/K_{IC}). Actual pressure vessels were then tested in low cycle fatigue and the agreement between predicted and observed failures was excellent. Although the extension of the fracture mechanics approach, which assumes the presence of defects in the structure, to time-dependent failures is a relatively new area for study, the initial results indicate that it does have considerable merit.

* C.F. Tiffany, *An Approach to the Prediction of Pressure Vessel Minimum Fatigue Life Based Upon Applied Fracture Mechanics*. Boeing Co. Report No. 02-22437, March 1963.

TABLE B-1

Properties of 5Cr-Mo-V Aircraft Steel (H-11)

Alloy:	5Cr-Mo-V		
Form:	All wrought forms		
Condition:	Heat treated (quenched and tempered) to obtain F_{TU} indicated.		
<i>Mechanical Properties:</i>			
F_{TU} , ksi			
L	240	260	260
T	240	260	280
F_{TY} , ksi			
L	190	205	220
T	190	205	220
K_{IC} , ksi $\sqrt{(in.)}$			
L	82	54	41

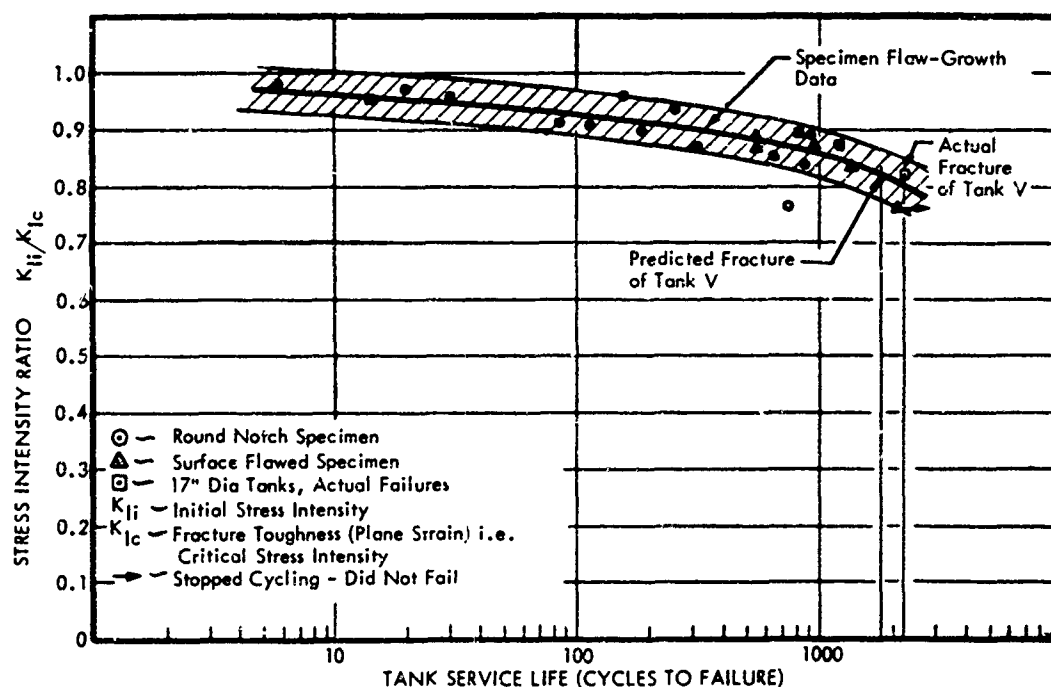


Fig.B-1 Prediction and verification of tank service life from specimen flaw-growth data (Tiffany)

DISCUSSION ON PAPER BY E.A. STEIGERWALD

Mr A.H. Priest described work on the effect of sulphur, phosphorus and silicon on the stress corrosion limit K_{ISCC} of a NiCrMoV steel determined by the B.F. Brown precracked beam test. The effect of silicon was included as this element gave rise to the 350°C intergranular type of embrittlement. The results showed that low S + P gave a high K_{ISCC} and a long period to fracture, whereas Si + S, Si + P and S + P (worst) all gave a low K_{ISCC} and a short time to failure. In the plots K_I versus time to failure, high S + P gave a concave curve, and low S + P a convex curve indicating a discontinuity in the change of crack growth rate with K_I . Changes in tempering temperature had little effect on the results, so S and P did not affect the tempering reactions. An analysis of the results showed that in fact Si had no effect and that it was the total S + P which was important. A plot of K_{ISCC} versus total S + P gave a concave curve. Mr Priest added that he thought the good K_{ISCC} properties of 9Ni4Co and 18Ni maraging steels were due to their low S + P content resulting from careful preparation of the metal. If high S + P were allowed into 18Ni steel, a low K_{ISCC} resulted.

Professor J. Nutting compared the results of K_{ISCC} tests in Dr Steigerwald's paper with results from Dr Baker's work at the British Welding Research Association on the influence of charged hydrogen on K_I versus time-to-failure. The two sets of results were very similar; specimens charged with hydrogen gave a K_I limit similar to K_{ISCC} . Now, susceptibility to hydrogen embrittlement depended on the microstructure; twinned martensite was very susceptible and untwinned not susceptible. There might therefore be a similar correlation between twinning and K_{ISCC} : if so, one should avoid steels whose strength was developed by twinning of the martensite.

The remainder of the discussion centred round the uses and significance of the fracture toughness approach. Mr Priest mentioned the importance of time-to-failure as well as K_{ISCC} limit; he had found En30B (4Ni1CrMo) and 9Ni4Co both to have a K_{ISCC} of 26 units, but at stress intensities just above this En30B failed in 30 minutes whereas 9Ni4Co took 1000 minutes to fail. He had also found that the critical limit was higher with a stress corrosion crack than with a fatigue crack, i.e. the fatigue crack was sharper. Micrographs of failed specimens showed the transgranular fatigue crack changing to an intergranular stress corrosion crack.

Mr L. Williams thought the precracked specimen very useful in stress corrosion work on high strength materials, but asked how useful it was on tougher materials. Dr Steigerwald thought this difficult to answer. For very tough materials a thick specimen must be used and the results were less quantitative. The method was still useful, however, in that, a stress raiser being present, the scatter of test results and the duration of tests were reduced. Mr H. Brooks wondered what the relation was between K_{ISCC} and the threshold stress data, determined on plain specimens, which could be used directly by designers. Dr Steigerwald knew of no correlation. The behaviour of smooth specimens depended on their size; threshold stress data were only significant if determined on specimens of the same thickness as the service components. Mr E.H. Phelps remarked that there was only a very approximate correlation between resistance to SCC and toughness. Some austenitic stainless steels were very tough but susceptible to SCC, and some low strength quite brittle steels did not suffer SCC in seawater. Dr Steigerwald agreed. Toughness correlated with resistance to SCC only within a given class of steel in a given environment. One could not measure K_{IC} for lower strength steels.

STRESS CORROSION CRACKING OF
HIGH STRENGTH STAINLESS STEELS

by

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SUMMARY

This paper is a review of the stress corrosion characteristics of high strength stainless steels with particular emphasis on aircraft applications. An attempt has been made to correlate laboratory test results with natural exposure and service behavior and, where possible, to suggest maximum stress levels for design considerations. The steels covered include the cold worked austenitic, the martensitic and the precipitation hardening types. Some typical aircraft applications of each are described. The mechanism of failure in the light of current theories is discussed including the metallurgical development of alloys for stress corrosion resistance. Protective measures and their effectiveness are reviewed.

STRESS CORROSION CRACKING OF HIGH STRENGTH STAINLESS STEELS

E. E. Denhard, Jr

1. INTRODUCTION

High Strength stainless steels have grown up with, and been a part of, the aircraft industry since the early days of flight. According to Ffield¹, two types of stainless (18-8 and 13Cr) were known to airship designers in 1928. His company, the Goodyear-Zeppelin Corporation, recognized that both had interesting possibilities but found the hardenable 13% chromium steel to be subject to stress corrosion cracking. Nevertheless, the British successfully used this alloy in the airship R 101 and, by ingenious fabrication and heat treating techniques, overcame the stress corrosion problem.

In 1935, Johnson² cited the advantages of cold worked 18-8 for metal aircraft, noting that "the percentage of wood and fabric in heavier-than-air-craft" was approaching the vanishing point. A decade later, Monypenny³ issued a warning on the dangers of using cold drawn 18-8 in aircraft construction, based on the observation that a severely strained hospital bowl of this grade failed in a relatively mild corrosive environment. This was promptly challenged by Franks⁴ who presented data showing that properly processed austenitic stainless steels were not subject to atmospheric stress corrosion. Thus, the stage was set for a controversy that has lasted twenty years and resulted in the initiation of countless investigations.

Today, large quantities of high strength stainless steel are used in many critical aircraft applications. Their acceptance is based on a combination of useful engineering properties and a high level of corrosion resistance. Ease of fabrication and economy are secondary, but also important.

With the increased use of these alloys, there has been a corresponding increase in the number of technical papers on stress corrosion cracking, with the result that a serious problem seems to be implied; yet reports of actual service failure attributable to this cause are few. One might justly ask, "Why all the concern?" Several reasons appear logical. Spectacular failure mechanisms become a popular subject for research, and stress corrosion cracking is certainly one of the most intriguing. Secondly, any failure in a critical application is undesirable and, in the case of aircraft, could be disastrous. Since aircraft are subject to the conditions that can cause stress corrosion, due to the nature of the environment in which they operate, it is essential that all of the factors that promote it be understood and controlled.

The first paper of this symposium covered the theoretical and practical aspects of stress corrosion cracking. Many of the concepts advanced apply to the high strength

stainless steels; however, since each metallic system has specific environments and metallurgical structures that, in combination, either resist or cause susceptibility to stress corrosion, a more detailed review would appear in order.

It appears that one of the most troublesome areas of stress corrosion is that of drawing conclusions based on the published data. The lack of standardized stress corrosion test methods has resulted in a host of data that defies comparison. How high can stainless steels be stressed and under what conditions? How do the laboratory tests compare with actual field experience? What is the metallurgical structure needed for resistance to stress corrosion and how can this be maintained through fabrication and manufacturing operations? How effective are protective measures? The purpose of this paper is to review each of the above areas and, where possible, present the latest position.

2. TYPES OF HIGH STRENGTH STAINLESS STEELS

The high strength stainless steels discussed in this paper are characterized by having a tensile strength of 150,000 lb/in² or higher. Basically, they are steels common to the United States although, for the most part, they have similar counterparts in other countries.

Table I lists the chemical composition of the principal high strength stainless steels used in aircraft and aerospace. This list was compiled by reviewing the AMS Index and Usage Survey⁵ and the technical literature. In addition to the grades shown in Table I, a small number of fabricators indicated that they used some of the free machining variations of the martensitic types. Typical mechanical properties are reported in Table II.

In referring to Table I, it may be noted that the high strength stainless steels fall into three categories:

- I. Austenitic (cold worked)
- II. Martensitic
- III. Precipitation hardening
 - A. Martensitic
 - B. Semi-Austenitic

The austenitic chromium-nickel stainless steels develop high strength as a result of cold work (either cold rolling or drawing) and are generally stress relieved at low temperatures (below 800°F) to achieve the best combination of strength and ductility. The alloys of principal interest are those whose metallurgical stability (high work hardening rate) favors the austenite-to-martensite transformation. These steels are limited to applications where joining or environmental temperature effects do not result in loss of strength, since they cannot be reheat treated to restore their mechanical properties. An excellent review article on the properties of cold rolled austenitic stainless steels is available⁶.

The martensitic stainless steels are essentially straight chromium alloys with or without small additions of other elements, principally columbium, nickel and molybdenum.

They derive their strength from a martensite transformation on cooling to room temperature from a high temperature austenitizing treatment. It is customary to use these alloys in a stress relieved or tempered condition. Type 410 (12% Cr) is the basic alloy, with the remaining 400 series representing important modifications.

The precipitation hardening stainless steels combine the excellent corrosion resistance of the austenitic chromium-nickel alloys with the heat hardening characteristics of the straight chromium grades. Basically, they are of two types: (i) martensitic and (ii) semi-austenitic. 17-4 PH*, FV-520(B) and PH 13-8 Mo are martensitic precipitation hardening alloys. In the solution treated condition, they possess moderate strength and formability. Low temper aging treatment (850-1150°F) temper the martensite and result in age hardening for improved mechanical properties.

Examples of the semi-austenitic precipitation hardening stainless steels include FV-520 (S), 17-7 PH, PH 15-7 Mo, AM-350 and AM-355. As annealed, these steels are soft and can be easily fabricated. Cold working or thermal treatments produce a martensitic matrix which, in the case of 17-7 PH, PH 15-7 Mo and FV-520 (S), respond to further age hardening by low temperature treatments. AM-350 and AM-355 use a final low temperature treatment to temper the martensite matrix. Considerable data are available on the physical metallurgy and mechanical properties of these alloys, some notable references being References 7, 8, 9, 10, 11 and 12.

3. APPLICATIONS

Excellent examples of the use of high strength stainless steel in aircraft are the 2000 mph, 265 ton, XB-70's built by North American Aviation. These planes required 20,000 square feet of brazed honeycomb panels fabricated from PH 15-7 Mo heat treated to a tensile strength of 190,000 lb/in². In addition, substantial portions of the substructure for the wings and fuselage were machined from heavy sections of 17-4 PH. AM-350 and AM-355 were used for the 4000 lb/in² hydraulic tubing and fittings. The aircraft is shown in Figure 1.

Fielding¹³ reported that FV-520 was selected as the principal construction material of the Avro 730 supersonic bomber and, although the project was later cancelled, it became the choice for the Blue Steel Missile which has since achieved operational status. Blue Steel is essentially an unmanned rocket airplane.

In less sophisticated aircraft, high strength stainless steels also find extensive use. Formed sheet metal sections of the semi-austenitic steels are used in hat and zee sections as stiffeners for panels and engine nacelles. These alloys also see service for tubular frames, welded sheet metal structures, formed bellows and springs.

Jet engines and secondary power equipment require substantial amounts of wire clips, snap-rings, shafts, bolts, levers and miscellaneous hardware. These are made from a wide selection of the hardenable stainless steels based on temperature and strength considerations.

Greek Ascoloy is used for turbine discs in the last stages of jet engines and Types 410, 17-4 PH and PH 13-8 Mo for compressor blades to combat corrosion from ingested salt laden moist air.

*Trademark Registered US Patent Office

Various hydraulic actuators and control assemblies have been manufactured from the martensitic precipitation hardening stainless steels and Type 431. The former have been widely used for high speed turbines, cast housing, and fuel control valves.

The more hardenable stainless steels (420, 440-A and 440-C) are generally restricted to nonstructural items but find applications in valve housings, wear pads, and for needle and spherical bearings.

4. TEST METHODS

A study of the technical literature on the stress corrosion cracking of high strength stainless steels reveals almost as many testing procedures as the number of steels studied. The result is that the data do not lend themselves to comparative analysis. This is due in part to the uncertainty of the mechanism (hydrogen embrittlement or stress corrosion) and the efforts of some investigators to accommodate both. The effects of the lack of standardization are discussed in the following sections.

4.1 Specimen Types and Application of Stress

Figures 2 and 3 represent the more common stress corrosion specimens and apparatus.

The constant deflection tests have found widest use in natural exposure, salt spray and high humidity environments. Bent beam specimens are relatively easy and cheap to prepare. They offer reasonably uniform stress patterns¹⁴, but exact failure time is difficult to determine because of the stress relaxation that results when cracking occurs. Horseshoe type specimens have similar advantages and disadvantages¹⁵.

In contrast, constant load tests find their greatest application in accelerated laboratory investigations. Strong acid media and toxic gases are conveniently contained in suitable enclosures. Failure time can be fairly accurately established because the unit stress increases once cracking commences and thereafter crack propagation and/or ductile fracture is rapid. This type of equipment is also readily adaptable for handling notched specimens for the purpose of introducing multiaxial stresses known to accelerate hydrogen embrittlement¹⁶⁻¹⁸.

4.2 Corrosive Media

The experimenter's complete freedom in selecting environments for stress corrosion testing is probably responsible for the bulk of the data that defies analysis. Table III lists some of the media which have been used to evaluate the stress corrosion resistance of high strength stainless steels. These may be grouped in three broad areas representing attempts to

- (i) reproduce conditions that exist during some part of the manufacturing, testing, and storage of parts,
- (ii) provide rapid laboratory screening data,
- (iii) simulate service conditions.

Each of these will be described in greater detail, but based on an analysis of tests performed by a number of investigators, the relative severity of the various media, as shown in Figure 4, appears reasonable.

4.3 Test to Determine Susceptibility During Parts Manufacturing, Testing and Storage

Comprehensive programs¹⁹⁻²¹ to determine if the fabricating processes and test methods used for high strength alloys could possibly account for subsequent stress corrosion damage are of interest.

In general, none of the high strength alloys tested (principally cold stretched Type 301 and heat treated precipitation hardened alloys) showed any susceptibility to stress corrosion cracking in any of the media shown in Section A of Table III, even when cold rolled or heat treated to very high strength levels. The solutions included commercial cleaning, deicing and paint stripping chemicals with varying pH. The superiority of the high strength stainless steels in these tests was evident compared to high strength low alloy steels and other alloy systems. Since the stainless steels were not affected by any of these media, no further comment on this subject will be made.

4.4 Accelerated Laboratory Stress Corrosion Tests

Various techniques have been developed to speed up the stress corrosion testing process.

Acid solutions poisoned with elements which promote the entry of hydrogen into the steel²²⁻²⁵ and cathodic charging^{26, 27} have been widely used to stress corrosion test the hardenable grades of stainless steel. In some instances, weak acid solutions saturated with hydrogen sulfide have been used. The optional addition of salt promotes pitting and hastens the process. These media have been popular with the petroleum industry, where serious embrittlement problems have been encountered in sour wells.

Suitable environments for accelerated testing of the cold worked austenitic alloys do not appear well established. There is some evidence that boiling 42% magnesium chloride and the hydrogen sulfide acid solutions referred to above may be useful for testing these materials.

In general, the accelerated tests shown in Section B of Table III produce cracking that varies in time from minutes to several hours. Under some conditions, specimens do not fail in days but general corrosion rates may be very high. The reproducibility of tests of this type is considered good. This is probably because the corrodent is in intimate contact with the metal surface as contrasted to the variable conditions of natural exposure.

4.5 Stress Corrosion Tests Simulating Service Conditions

Exposure of stressed samples to high humidity air, alternate wet and dry salt solutions, salt fog, marine, industrial and rural atmospheres are all attempts to simulate natural service conditions. The relative severity of the environments has been debated. One investigation reported salt spray to be most severe, followed by coastal marine exposure and alternate immersion²⁸. The severity of natural exposure is affected

by the time of the year specimens are placed in test, the temperature, rainfall and probably a host of other factors. In marine atmosphere, the deposition of air-borne salt water with alternate wetting and drying conditions is a potent factor in causing stress corrosion cracking.

5. TEST DATA AND BEHAVIOR IN SERVICE

The relative stress corrosion resistance of the high strength stainless steels is extremely difficult to assess, for reasons described earlier. However, an attempt has been made to indicate the maximum safe applied stress for each alloy classification as determined by a review of the published data. This is shown in Figure V. It is based on exposure to a severe marine atmosphere such as might be encountered in aircraft carrier operation. This chart is only intended as a rough guide, since actual service performance may vary considerably, as described in the following sections.

5.1 Cold Worked Austenitic Alloys

The high strength, cold worked chromium-nickel stainless steel alloys offer an interesting comparison between accelerated laboratory, natural exposure, and field experience.

Matsushima, Deegan and White²⁹ showed that annealed Type 301 failed in 17 minutes in boiling 42% magnesium chloride. With successive degrees of cold work the cracking time became progressively shorter until, with 40% reduction, a life of only 5 minutes was realized.

These results are contradictory to those obtained by workers in my laboratory. Figure 6 shows the results of previously unpublished data from our tests with the above superimposed for comparison. Matsushima used a constant spring loaded "C" type specimen with an applied stress beyond the elastic limit. Our tests had a uniform applied tensile stress of 25,000 lb/in². It is interesting to note that we showed Type 305 (18 Cr-11 Ni) to be superior to Type 301 in the annealed condition (due to the higher nickel content) but inferior after cold working.

In contrast to the above accelerated tests, full hard Type 301 samples stressed to 75% of the 0.2% yield strength (180-202,000 lb/in²) did not fail in 400 days of marine exposure at Kure Beach, North Carolina³⁰. Twenty percent salt spray, alternate immersion and industrial atmospheric exposures displayed equally good results. Excellent atmospheric stress corrosion resistance for the austenitic stainless steels has also been reported by others³¹. Samples stressed to their 0.1% proof stress after various degrees of cold work withstood over three years' exposure to a heavily polluted industrial atmosphere without any indication of cracking.

Apparently, cold worked austenitic alloys can be cracked in relatively short times in media such as boiling magnesium chloride, but they are highly resistant to all types of atmospheric corrosion and simulated service conditions. These data also show the fallacy of predicting behavior in natural environments, based on accelerated laboratory type tests. No literature references were found of actual service failures and it can only be concluded that this class of alloys has excellent resistance to stress corrosion for most applications.

5.2 Martensitic Alloys

The martensitic stainless steels display varying degrees of susceptibility to stress corrosion cracking, depending largely on heat treatment, alloy content and exposure conditions.

Table IV shows the cracking time of Type 410 hardened and tempered at various temperatures, and exposed to various media. The applied stress was 100,000 lb/in², except where indicated otherwise. Photomicrographs of Type 410 fractures in several media are shown in Figures 7 and 8. These pictures illustrate that cracking may be intergranular or transgranular depending on environment.

It is apparent that the choice of corrosive environment has a pronounced effect on failure time. Moreover, it appears that tests conducted under constant load fail more rapidly than those stressed to the same level but under constant deflection conditions. Acid media produce very short failure times but, in general, distinguish between susceptible and nonsusceptible metallurgical conditions. With weaker acid solutions or with salt spray, cracking time becomes longer, until in industrial atmospheres cracking does not occur or takes exceptionally long.

Martensitic stainless steels tempered between 340°C (650°F) and 540°C (1000°F) are subject to rapid failure in most environments^{26, 32, 33}. Stress relieving at temperatures less than 340°C (650°F), or tempering at temperatures over 540°C (1000°F), results in significantly better performance. Of these two conditions, stress relieving offers the highest strength, but a threshold cracking stress as low as 45,000 lb/in² has been noted for a 0.19 C-12Cr steel heat treated to the 220,000 lb/in² strength level¹⁸. Thus, for critical applications, highly tempered conditions should be considered. Tempering Type 410 at 565°C (1050°F) produces a 0.2% yield strength in excess of 100,000 lb/in² and appears to offer immunity to marine stress corrosion cracking even when stressed at 70,000 lb/in². Truman and Kirkby³¹ see little hazard when the martensitic steels are used at ultimate tensile strengths below 150,000 lb/in².

In general, the susceptibility of the hardenable straight chromium grades increases with carbon content¹⁸. For the same tempering temperature and applied stress, the more hardenable grades (Types 420, 440-A and 440-C) are less resistant and greater caution must be exercised in their application³³.

Alloying additions to 12Cr steels result in improved performance. Types 431 (Ref. 34), 414, Greek Ascoloy, 422 (Ref. 32) and FV-448 (Ref. 18) all show better resistance to stress corrosion than Type 410. The more resistant of this group, Greek Ascoloy, Type 422 and FV-448, appear fully resistant when heat treated to a tensile strength of 160,000 lb/in² and stressed to 90,000 lb/in². In this condition, no problems would be anticipated in severe marine atmospheres or humid tropical environments that aircraft encounter.

Actual service failures of the martensitic stainless steel reported in the literature are few. Noble and Sharp³² mentioned an early failure of a Type 414 (13 Cr-2 Ni) tie-rod used to hold the discs and spacers of a jet engine together. Failures of 12Cr jet engine compressor blades were found to be caused by stress corrosion cracking³⁵. Accelerated laboratory stress corrosion tests showed that tensile stresses of 50,000 lb/in² were sufficient to cause cracking if the material was tempered below 500°C (950°F). By tempering the blades at a higher temperature, failure were prevented.

Several years ago, some Type 431 jet engine poppet valve assemblies which had failed in service came to the attention of our laboratories. These handled jet engine fuel and reportedly operated at temperatures as high as 230°C (450°F). The failures appear to be caused by stress corrosion but there was insufficient information available to pinpoint the cause. The parts were originally in the hardened and stress relieved condition. As far as we know, hardening and tempering at 1200°F solved this problem.

5.3 Precipitation Hardening Alloys - Martensitic

The precipitation hardening stainless steels have been extensively stress corrosion tested in environments varying from those encountered during fabrication to simulated service conditions. There seems to be no doubt that this class of alloys offers useful engineering properties over and above what can be expected of the martensitic stainless steels, particularly where stress corrosion resistance is concerned.

Table V illustrates the effect of environment on 17-4 PH. As with the straight chromium martensitic alloys, cracking can occur rapidly in strong acid media for some heat treated conditions. It is important to note, however, that stress corrosion resistance is markedly improved with higher aging temperatures. This characteristic was not always shared to the same extent by the hardenable straight chromium alloys under the severe conditions of an acid environment and constant load testing. Figure 9 illustrates the misleading effect laboratory tests may have on predicting behavior. Acid media showed a dip for specimens aged at 550°C (1025°F) but marine atmospheric specimens were most susceptible aged at 482°C (900°F).

The atmospheric stress corrosion resistance of 17-4 PH is significantly better than the 12Cr type alloys, particularly in the 480°C (900°F) - 540°C (1000°F) tempering/aging range where the most desirable mechanical properties are obtained. For most applications, aging to maximum strength is not recommended, a slight sacrifice being preferred to assure immunity to stress corrosion in questionable applications.

Excellent stress corrosion resistance was also reported for FV-520(B) (Ref.7). No failures have occurred in 17,000 hours in a heavily polluted industrial atmosphere with an applied stress of 150,000 lb/in².

Welding decreases the stress corrosion resistance of 17-4 PH in the stronger heat treated condition³⁰. Full hard specimens (200,000 lb/in² ultimate tensile strength) exposed 80 feet from the ocean with an applied stress of 160,000 lb/in² showed the following results:

Condition	Failure Time (days)
Unwelded	573
Weld + Solution Treat + Age	68
Solution Treat + Weld + Age	20

Unwelded specimens aged at 550°C (1025°F) and higher and those solution treated after welding and aged in this manner have not failed in 6½ years of continuous exposure.

Based on published data and considerable user experience, an applied stress of 150,000 lb/in² appears safe for 17-4 PH heat treated to Condition H 1025 (165,000 lb/in² yield strength). Data on the stress corrosion resistance of 17-4 PH and other martensitic precipitation hardening alloys are given in References 27, 30 and 33.

Two new martensitic precipitation hardening stainless steels, 15-5 PH and PH 13-8 Mo (Ref.36), are of interest. The former was developed to provide a ferrite-free version of 17-4 PH with improved forgeability and transverse properties. Stress corrosion data on this alloy are being accumulated. It appears to be similar to 17-4 PH.

PH 13-8 Mo is a ferrite-free aluminum bearing precipitation hardening stainless steel that responds to either single or double heat treatment. It was developed to be compatible with the semi-austenitic precipitation hardening alloys and can be joined to the latter with brazing or welding operations that permit high strength sheet metal and heavy section assemblies. Stress corrosion tests on PH 13-8 Mo are in progress. Data obtained to date indicate it is the most resistant of the martensitic precipitation hardening alloys and is capable of sustaining higher stresses without cracking. A summary of properties is shown in Table VI.

Large quantities of the martensitic precipitation hardening stainless steels have been used in aircraft applications with exceptionally fine performance. Failures attributed to stress corrosion cracking have been almost non-existent. Where cracking has occurred, obvious metallurgical reasons have been found and could have been anticipated. For example, a failed 17-4 PH bolt, exposed to coastal atmospheres, was found "underaged" and structurally embrittled; the heat treatment appeared to be somewhat less than the preferred 496°C (925°F)-510°C (950°F) for high strength applications.

It should be mentioned in passing that there have been a large number of investigations on the stress corrosion characteristics of the martensitic precipitation hardening alloys directed to use in nuclear power plants. In these applications, the 290°C (550°F) operating conditions are far different from those experienced by aircraft. However, even here, 17-4 PH remains a preferred material for critical control drive and pump construction, where wear and stress corrosion resistance are needed in combination with high strength.

5.4 Precipitation Hardening Alloys - Semi-Austenitic

Like the other classes of alloys discussed, the data on the stress corrosion characteristics of the semi-austenitic precipitation hardening stainless steels are too voluminous to cover in any more than a general way. Attention is directed to some of the excellent references on this subject^{27, 30, 33}.

The metallurgy of the semi-austenitic precipitation hardening alloys is somewhat complicated and stress corrosion resistance varies considerably with the sequence of cold working and/or thermal treatments.

The schedule below outlines the most common treatments for 17-7 PH and PH 15-7 Mo:

Condition	Austenite Conditioning	Transformation	Age
TH 1050	760°C (1400°F)	Cool to 16°C (60°F)	565°C (1050°F)
PH 950	950°C (1750°F)	-73°C (-100°F)	500°C (950°F)
CH 900	-	Cold roll	480°C (900°F)

Comparative stress corrosion data indicate that PH 15-7 Mo is more resistant than 17-7 PH and that the TH condition is more resistant than the RH. In severe marine atmospheres, a limiting applied stress of 80-90,000 lb/in² is suggested for materials so treated if failure is to be avoided. The CH condition is considerably more resistant, and stresses of 200,000 lb/in² or more have been sustained 800 feet from the ocean for more than two years, and in 20% salt fog for more than one year.

AM-350 and AM-355 are similar to 17-7 PH and PH 15-7 Mo, but have somewhat differing heat treatments. The heat treating schedule for these alloys is as follows:

Condition	Austenite Conditioning	Transformation	Temper
SCT 850	930°C (1710°F)	-79°C (-110°F)	454°C (850°F)
SCCRT 850	-	Sub-zero cooled, cold roll	454°C (850°F)
CRT 850	-	Cold rolled	454°C (850°F)

AM-350 appears more resistant to stress corrosion than AM-355 (Ref. 28) and the CRT condition offers greater immunity than the SCT or SCCRT conditions. In this respect, the suggested safe stress levels for 17-7 PH and PH 15-7 Mo appear applicable to these alloys, with the exception of the SCT condition, which is more susceptible. Specimens of AM-350 and AM-355 stressed at 140-150,000 lb/in² failed in an average time of 110 days in the Los Angeles atmosphere when heat treated to this condition.

Recently, a new heat treating sequence was proposed for AM-355 (Ref. 37) which offers improved stress corrosion resistance. This treatment involves a 1063°C (1950°F) anneal and refrigeration cycle ahead of the SCT condition. Samples so treated with a final temper of 540°C (1000°F) have sustained 313 days in 5% salt fog under a stress of 165,000 lb/in².

Stress corrosion data on FV-520(S) were not available for tests under the same conditions as the alloys referred to above. However, the mechanical properties and methods of obtaining them are similar to 17-7 PH and PH 15-7 Mo and, in this regard, the same principles regarding stress corrosion performance would appear reasonable.

Generally speaking, several fixed heat treated conditions are offered by the producers of these steels for the purposes of establishing guaranteed minimum properties, but the basic principle of using overaged material for maximum stress corrosion resistance should not be overlooked. For critical applications, the rule should be: use the highest aging temperature that yields properties compatible with design requirements.

PH 14-8 Mo (Ref. 53) is a relatively new semi-austenitic precipitation hardening stainless steel that promises superior stress corrosion resistance. This is demonstrated by the following data which compare this alloy with 17-7 PH and PH 15-7 Mo, its evolutionary predecessors.

Marine Exposure - Kure Beach, North Carolina

Alloy	Condition	0.2% Yld. Str. (ksi*)	Exposure Stress (ksi)	Days to Failure
17-7 PH	PH 950	203,000	181,000	1
PH 15-7 Mo	RH 950	202,000	182,000	12
PH 14-8 Mo	SRH 950	225,000	180,000	No failure in 1100

* ksi = 1000 lb/in²

The results of these tests are all the more remarkable because 17-7 PH and PH 15-7 Mo were exposed in the longitudinal direction and PH 14-8 Mo was transverse. This class of steels, like other alloys, shows inherently poorer stress corrosion resistance when specimens are tested transverse to the rolling direction.

No cases of stress corrosion failures were found in the literature on aircraft applications for these alloys. Two items that came to my attention involved PH 15-7 Mo and AM-355 but the former was attributed to careless handling during pickling and the latter to leaving spot welded sheet metal assemblies in the as-welded condition.

6. MECHANISM OF FAILURE

It is difficult to define the stress corrosion failure mechanism of the family of high strength stainless steels in any more than general terms because of the complexity of structures and the unique relationship of each to specific conditions. The most commonly accepted idea is that cracking is the result of hydrogen embrittlement or accelerated corrosion along a crack-sensitive path such as a grain boundary. In recent years, the concept of fracture mechanics in conjunction with a corrosion process has gained momentum. This approach suggests that once a pit or stress raiser is originated by a relatively slow corrosion process, a critical size flaw is generated, which propagates rapidly to cause complete failure²⁵. Within the last year, there have been several proposals^{29, 31} that stress corrosion cracking of the relatively weak and highly ductile austenitic chromium-nickel stainless steels might also be a manifestation of hydrogen embrittlement, not unlike that of the hardenable grades. These alloys furnish a convenient system for study because of their structural change after cold working.

The problem of analyzing the mechanism of failure is not simple. The possibility of several mechanisms being operative within a given alloy system has been considered^{17, 18} and appears to have merit.

The relative immunity to stress corrosion cracking of the highly cold worked austenitic alloys apparently has hampered efforts to analyze the mode of failure in this class of alloys. Data in the technical literature are conspicuous by its absence. The work of Matsushima et al.⁴⁰ suggests that the body center cubic structure of transformed austenite is susceptible to hydrogen embrittlement and is presumably the cause of failure.

Our laboratories have found that the crack characteristics of the austenitic stainless steels change with cold work. Stress corrosion tests on Type 301 in boiling 42% magnesium chloride described earlier showed highly branched cracking for annealed material. With increasing cold reduction (up to 40%), the time to failure increased six-fold and the cracks became fewer and straighter. The latter closely resemble failures of the hardenable stainless steels under conditions that cause hydrogen embrittlement.

The 400 series of martensitic alloys offers metallurgical conditions that are thought to be susceptible to either stress corrosion or hydrogen embrittlement. For example, Type 410, hardened and tempered at temperatures up to about 500°C (950°F) appears to be susceptible to hydrogen embrittlement and fractures are predominantly

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No cases of stress corrosion failures were found in the literature on aircraft applications for these alloys. Two items that came to my attention involved PH 15-7 Mo and AM-355 but the former was attributed to careless handling during pickling and the latter to leaving spot welded sheet metal assemblies in the as-welded condition.

6. MECHANISM OF FAILURE

It is difficult to define the stress corrosion failure mechanism of the family of high strength stainless steels in any more than general terms because of the complexity of structures and the unique relationship of each to specific conditions. The most commonly accepted idea is that cracking is the result of hydrogen embrittlement or accelerated corrosion along a crack-sensitive path such as a grain boundary. In recent years, the concept of fracture mechanics in conjunction with a corrosion process has gained momentum. This approach suggests that once a pit or stress raiser is originated by a relatively slow corrosion process, a critical size flaw is generated, which propagates rapidly to cause complete failure²⁵. Within the last year, there have been several proposals^{29, 33} that stress corrosion cracking of the relatively weak and highly ductile austenitic chromium-nickel stainless steels might also be a manifestation of hydrogen embrittlement, not unlike that of the hardenable grades. These alloys furnish a convenient system for study because of their structural change after cold working.

The problem of analyzing the mechanism of failure is not simple. The possibility of several mechanisms being operative within a given alloy system has been considered^{17, 18} and appears to have merit.

The relative immunity to stress corrosion cracking of the highly cold worked austenitic alloys apparently has hampered efforts to analyze the mode of failure in this class of alloys. Data in the technical literature are conspicuous by its absence. The work of Matsushima et al²⁹ suggests that the body center cubic structure of transformed austenite is susceptible to hydrogen embrittlement and is presumably the cause of failure.

Our laboratories have found that the crack characteristics of the austenitic stainless steels change with cold work. Stress corrosion tests on Type 301 in boiling 42% magnesium chloride described earlier showed highly branched cracking for annealed material. With increasing cold reduction (up to 40%), the time to failure increased six-fold and the cracks became fewer and straighter. The latter closely resemble failures of the hardenable stainless steels under conditions that cause hydrogen embrittlement.

The 400 series of martensitic alloys offers metallurgical conditions that are thought to be susceptible to either stress corrosion or hydrogen embrittlement. For example, Type 410, hardened and tempered at temperatures up to about 500°C (950°F) appears to be susceptible to hydrogen embrittlement and fractures are predominantly

transgranular²⁶. Above this temperature, at least in some media, the fracture path becomes intergranular and is termed stress corrosion cracking. In this case, a crack-sensitive path is thought to be provided by the precipitation of chromium carbides, producing an iron-enriched route for electrochemical dissolution.

Phelps and Loginow²⁷ considered the mechanism of stress corrosion in 12% chromium steels to be the result of corrosion along an active path, and presented data to show that only under conditions of strong cathodic impressed current densities was fracture transgranular, and thus characteristic of hydrogen embrittlement. Their work was carried out on specimens tempered at 425°C (800°F). Studies at lower stress relieving temperatures might be informative.

Invariably, investigators have found cracking to be associated with pitting. Fontana³⁴ noted that cracks emerged from deep pits in Type 403 (12 Cr) but that, at higher tempering temperatures where crack sensitivity was lowered, the pits were hemispherical. These observations appear to tie in with Hoke's²⁵ findings that fracture toughness and stress corrosion (or stress-hydrogen) cracking are related in the brittle failure mechanism. Possibly, the stress concentration at the base of hemispherical pits is too low to initiate and propagate cracks.

The mechanism of failure of martensitic stainless steels has not been settled. Perhaps it has been confused by the variety of test methods employed to study the phenomenon. From the standpoint of failure during actual operating conditions, that is, natural environments, the mechanism is not any easier to define. Most of the failures that I have examined that occurred in marine atmospheres appeared to be intergranular and of a stress corrosion nature. On the other hand, there have been examples of cracked parts, that, due to the environment (pickling and plating) or because of galvanic coupling with less noble materials, strongly suggest hydrogen embrittlement to be the cause.

The precipitation hardening stainless steels generally appear to stress corrosion crack by mechanisms similar to those reported for the martensitic straight chromium alloys. Because of their unique hardening processes, however, certain differences may be noted. For example, when hardening is accomplished by cold rolling and aging, as in the case of 17-7 PH (Condition CH 300), time to failure is longer than when the strength is obtained solely by thermal treatments. This is attributed to the compressive stresses imparted during the cold reduction and subsequent stress relieving (and simultaneous hardening) aging treatment. The fact that transformation is caused by cold working, and final aging is generally in a temperature range lower than that required to cause profuse carbide precipitation (as in the TH condition), lessens the possibility of a crack-sensitive path.

The environment may be as important as the metallurgical condition insofar as the mechanism of failure is concerned. For example in Table V, 17-4 PH cracks rapidly in the acid-salt-hydrogen sulfide solutions regardless of aging temperature. In the hydrochloric acid-selenium dioxide solution, however, near immunity seems to be achieved by aging at 593°C (1100°F) - 620°C (1150°F). Both solutions are thought of as hydrogen embrittling but it is possible that the salt solution also offers the additional possibility of stress corrosion cracking.

It is possible that the mechanism is further complicated by the inherent general corrosion resistance of the alloy being studied. For example, 17-4 PH aged at 593°C (1100°F) did not display the resistance to the 10% HCl solution that was exhibited by 17-4 PH aged at 6. C (1150°F).

7. METALLURGICAL DEVELOPMENT FOR RESISTANCE TO FAILURE

The mysteries of stress corrosion are far from understood, but enough progress has been made in metallurgical developments to use them to good advantage.

Areas which deserve special comment are (1) alloying and chemistry control, (2) melting techniques, and (3) fabrication and heat treating sequences.

7.1 Alloying and Chemistry Control

The significant improvement in the performance of 12% chromium alloys afforded by small alloy additions is a matter of record^{18, 26, 32}. Noble and Sharp³² concluded that the alloys that have the highest hardness for a given tempering temperature are generally most resistant to stress corrosion cracking. Possibly a disproportionately higher relief of internal stresses is achieved in these steels without sacrificing useful strength. Small additions of columbium, vanadium, molybdenum and tungsten are particularly effective in promoting this characteristic. These elements retard coalescence of carbides by diffusion at tempering temperatures. It should not be overlooked that some of these elements contribute to control of grain size, thus further delaying failure due to the circuitous route a potential crack must follow. An excellent example of the latter is the beneficial effects of only 0.15% columbium to Type 316 (Ref. 40). Molybdenum apparently improves the stress corrosion performance of the high strength stainless steels by increasing their pitting resistance and inhibiting tempering. Carbon is perhaps the most influential element - low carbon being preferred in most cases. The literature^{18, 33} is replete with examples of lower carbon steels outperforming their higher carbon counterparts.

The precipitation hardening stainless steels combine in a practical way the observations of Noble and Sharp with a simultaneous strengthening mechanism, thus offering higher useful strengths. Even here, an evolutionary process is in progress and several new steels (PH 13-8 Mo and PH 14-8 Mo) have emerged, the impetus being provided largely by the aircraft industry.

As the newer steels evolved, the accent was frequently on improved toughness at high strength levels but, happily, this was found to benefit stress corrosion resistance. As mentioned earlier, there seems to be a parallel between fracture toughness and stress corrosion resistance in the newer alloys. A similar relationship was noted between impact strength and stress corrosion characteristics noted for the older 13% chromium steels.

There is also a trend toward restricting all elements not considered essential for the alloy's total performance. Perry¹⁹ found that small amounts of sulfur, lead, arsenic, antimony and tin have an adverse effect on the stress corrosion resistance of 13% chromium steels. The restrictive chemistry of PH 13-8 Mo (Ref. 36) and PH 14-8 Mo (Ref. 38) also reflects this direction. Sulfur in particular seems to be harmful.

Several investigators^{34, 41} have noted that chloride ions are attracted to inclusions of this element and the corrosive attack which results serves as a nucleus for cracking.

7.2 Melting Methods

The melting process is generally governed by the economics and the final chemistry specified. There are little data reported to show that it has any direct effect on stress corrosion resistance but there seems to be a growing feeling that it is important. Vacuum induction melting and consumable electrode vacuum remelting processes are the principal methods of interest.

The high vacuum and pure materials used in most vacuum induction processes produce exceptionally clean steels. Nonmetallic inclusions are preferred locations for pitting and localized attack, both of which appear to be associated with stress corrosion cracking. Furthermore, vacuum melting reduces gas content which, in the case of nitrogen, has been found to be detrimental in at least one high strength stainless steel³⁸.

Consumable electrode vacuum remelting retains the advantages gained in the above process. In addition, it reduces segregates and changes the solidification process to offer steels with improved transverse properties, particularly for larger section sizes.

7.3 Effect of Fabrication and Heat Treating Sequence

Unless care is exercised in planning the sequence of fabrication steps, including welding and heat treating, the useful properties of the high strength stainless steels are not realized.

Generally speaking, the operational steps must be such that residual stresses are held to a minimum. Garvin⁴² investigated the effect of heat treating sequence on the residual stresses in 17-4 PH. It was found that the highest aging temperatures offered the greatest stress relief and that fabrication preferably should be performed on material in the solution treated condition. Residual stresses were lower for material so processed compared to that which was fabricated in the aged condition and subsequently reaged.

Fit-up for welding and joining has been considered a prime source of high internal stresses⁴³. Due to the high elastic modulus of steels, small variations in deformation to accommodate misfit may account for sizeable stress patterns. The relief of these stresses by post-weld tempering or aging treatments is extremely helpful in preventing failure in use.

Stress corrosion cracking of welded martensitic and precipitation hardened stainless steels tends to preferentially occur in the heat affected zone adjacent to the weld. Carbide precipitation associated with this area provides a susceptible region for corrosive attack which, when combined with high tensile stresses, fails intergranularly. Pre-aging or tempering before welding minimizes this type of attack by reducing the gradient of intergranular precipitates. Additional tempering or aging after welding is highly desirable to minimize the internal stresses produced during this operation.

8. PROTECTIVE MEASURES AND THEIR EFFECTIVENESS

Since stress corrosion is the result of the interplay of a corrosion process and stress, it follows that, by limiting either of these elements, immunity can be achieved. Logically, this starts with proper design and alloy selection, but there are other practical approaches that can be taken.

8.1 Painting and Protective Coatings

Barriers between the environment and the metal surfaces provide an effective means of controlling corrosion. Despite the high level of corrosion resistance of stainless steels, crevices, sharp fillets, rough surfaces, and contact with dissimilar metals provide excellent sites for localized corrosive attack.

Vacuum cadmium plating of Type 431 rivets in conjunction with manganese dioxide or chromate type flexible sealants was found particularly effective for protecting aircraft skin fasteners²⁶. Coatings that are anodic to the metal surface provide protection, those that are cathodic do not²⁷. To be effective, metallic coatings must be in electrical contact with the metal surface they are to cathodically protect. When vehicles with dielectric characteristics are used for suspension of metal particles, the efficiency of the protective process may be impaired.

One of the possibilities to be considered in using protective metallic coatings is that of hydrogen embrittling the metal to be protected. This hazard is theoretically present since, in a galvanic couple, the sacrificial coating becomes the anode and the part to be protected becomes the cathode. If the system is active and the coating is doing its job, the hydrogen evolving from the corrosion cell may be absorbed into the high strength steel, resulting in cracking. Apparently, this condition does not occur to any great extent in practice since no failures were noted in the literature that were attributed to this cause. Possibly, under natural conditions, absorption of a sufficient quantity of hydrogen to cause embrittlement is too slow.

Coatings that simply furnish a barrier between the metal surface and the environment (such as organic coatings) are useful if they remain intact, adherent and non-porous. Protective systems of this type should be fully resistant to crazing and cracking, or localized sites for corrosion may develop which can be more dangerous than leaving the metal unprotected. A further disadvantage is that the corrosion process may proceed undetected beneath the protective coating.

8.2 Shot-Peening

Changing the nature of the stress pattern by shot-peening or blasting is a very effective deterrent to stress corrosion cracking. Hildebrand et al⁴⁵, found that this procedure offered the best safeguard when even a remote possibility of this form of metal failure is anticipated. Shot-peening has been effective on helical and flat leaf springs, rotating equipment, and most structural parts.

Shot-peening of stainless steels should be performed with stainless steel shot or glass beads. The use of mild steel or other non-corrosion resistant materials may leave a surface contaminated layer which, in service, may rust and be the cause of stress corrosion or hydrogen embrittlement.

9. CONCLUSIONS

- (i) Accelerated laboratory stress corrosion tests are useful for screening and development purposes but cannot be used reliably for predicting behavior in service. Tests of this type may fail candidate materials that show no stress corrosion susceptibility in severe natural environments.
- (ii) Cold worked austenitic stainless steels have excellent stress corrosion resistance even at strength levels in excess of 200,000 lb/in².
- (iii) The chromium martensitic stainless steels are quite susceptible to stress corrosion cracking when tempered at 340°C (650°F) - 540°C (1000°F). In this condition, some of the higher carbon alloys appear to have a threshold cracking stress as low as 40,000 lb/in². Stress relieving below 340°C (650°F) or tempering above 565°C (1050°F) greatly improves their stress corrosion resistance, the latter being preferred. Applied stresses of 70-80,000 lb/in² appear safe for material so treated for most aircraft applications. The more highly alloyed martensitic steels allow stressing to even higher levels.
- (iv) Martensitic precipitation hardening alloys display excellent stress corrosion resistance in marine and industrial atmospheres. An applied stress of 150,000 lb/in² appears perfectly safe for material heat treated to a yield strength of 165,000 lb/in².
- (v) Semi-austenitic precipitation hardening stainless steels have stress corrosion characteristics that are similar, but somewhat superior, to the martensitic chromium alloys when their mechanical properties are produced by thermal treatments. When transformation is accomplished by cold working, the aged product more closely resembles the high strength austenitic alloys and unusually high stress corrosion resistance is available.
- (vi) The failure mechanism for high strength stainless steels is considered to be either hydrogen embrittlement or stress corrosion (accelerated corrosion along a crack sensitive path). The former seems likely for material tempered or aged at temperatures below 510°C (950°F) - 540°C (1000°F); the latter at higher temperatures where carbide precipitation becomes more pronounced. This trend is greatly affected by environment which may favor either mechanism. A correlation seems to exist between fracture toughness and stress corrosion resistance, both of which benefit from high-purity melts.
- (vii) Shot-peening and anodic metallic coatings offer useful protective methods for preventing stress corrosion.

Despite the large number of papers dealing with stress corrosion cracking of high strength stainless steels, the number of reported failures in aircraft applications are few. With a few precautions, this family of alloys offers extremely useful engineering properties which are not seriously impaired by environment.

The published data on the stress corrosion cracking of these steels are based on a wide variety of specimen types, environments, and stress levels which make comparison very difficult. There is a definite need for standardization in this area.

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TABLE I

Chemical Composition of High Strength Stainless Steels

Grade	C	Mn	Si	Cr	Ni	Mo	Cu	Others
301	0.10	1.25	0.50	17.5	7.0	-	-	-
410	0.12	0.50	0.35	12.0	-	-	-	-
420	0.35	0.50	0.35	13.0	-	-	-	-
422	0.20	0.50	0.35	13.0	-	1.0	-	W - 1.0
431	0.15	0.50	0.35	16.0	2.0	-	-	V - 0.25
440-C	1.00	0.50	0.50	17.0	-	-	-	-
Greek Ascoloy	0.15	-	-	13.0	2.0	-	-	W - 3.0
FV-448	0.10	1.00	0.40	11.0	-	0.8	-	Cb - 0.40 V - 0.15
17-4 PH	0.04	-	-	16.0	4.0	-	3.3	Cb - 0.25
FV-520 (B)	0.04	-	0.50	14.0	5.4	1.8	1.6	Cb - 0.50
15-5 PH	0.04	-	-	15.0	5.0	-	3.2	Cb - 0.25
PH 13-8 Mo	0.04	0.10 Max	0.10 Max	13.0	8.0	2.2	-	Al - 1.0, P - 0.01 Max, S - 0.008 Max, N - 0.01 Max
17-7 PH	0.07	0.50	0.30	17.0	7.0	-	-	Al - 1.0
PH 15-7 Mo	0.07	0.50	0.30	15.0	7.0	2.2	-	Al - 1.0
PH 14-8 Mo	0.03	0.10 Max	0.10 Max	15.0	8.4	2.2	-	Al - 1.0, P - 0.01 Max, S - 0.008 Max, N - 0.01 Max
AM-350	0.10	0.75	0.30	16.5	4.3	2.7	-	N - 0.10
AM-355	0.13	0.75	0.30	15.5	4.3	2.7	-	N - 0.10
FV-520 (S)	0.06	1.00	0.30	15.7	5.4	1.8	2.0	Ti - 0.2 Max

TABLE II

Typical Mechanical Properties of High Strength Stainless Steels

Grade	Ultimate Tensile Strength (ksi) [†]	0.2% Yield Strength (ksi) [†]	% Elongation in 2 in.	Condition*
301	260	244	1.5	CR 65%
	181	150	12.0	CR 40%
410	195	153	15.0	1800 + 600
420	230	195	8.0	1850 + 600
422	275	185	10.0	1900 + 800
431	200	140	15.0	1900 + 600
440-C	285	275	2.0	1900 + 600
Greek Ascoloy	210	180	12.0	1750 + 600
FV-448	193	142	11.5	1830 + 930
17-4 PH	200	185	14.0	1925 + 900
FV-520 (B)	180	150	12.0	1750 + 850
15-5 PH	200	185	14.0	1925 + 900
PH 13-8 Mo	255	200	13.0	1700 + 950
17-7 PH	235	220	6.0	1750 + (-100) + 950
PH 15-7 Mo	240	225	6.0	1750 + (-100) + 950
PH 14-8 Mo	230	215	6.0	1700 + (-100) + 950
AM-350	192	148	12.0	1750 + (-110) + 750
AM-355	215	182	18.0	1750 + (-110) + 750
FV-520 (S)	197	168	9.0	1925 + (-95) + 850

* Temperatures given in degrees F.

[†] ksi = 1000 lb/in.²

TABLE II:

**Environments Selected for Stress Corrosion Testing
High Strength Stainless Steels**

A. Media used during Parts Manufacturing, Testing and Storage

Trichloroethylene
 4% Soluble Oil Solution
 1% Marquench Salt Solution (Nitrates and Nitrites)
 1/2% Sodium Dichromate Solution
 Rust Inhibiting Oil
 Deicing Fluid Mil-D-19418
 Paint Stripper Mil-R-8633A
 Cleaning Solution Mil-C-25542
 IM Solutions - Sodium Nitrate, Sodium Sulfate, Sodium
 Phosphate and Sodium Sulfide

B. Accelerated Laboratory Media

18% HCl + 1% SeO₂
 1/2% H₂SO₄ + 3 mg/l As
 4% HCl + 3 NaCl + 20 mg/l As
 1/2 HAc + H₂S
 1/2 HAc + 6 NaCl + H₂S
 42% MgCl₂ (boiling)

C. Media Simulating Service Conditions

Air - High Humidity
 3-5-20% Salt Spray
 Marine
 Industrial
 Rural
 Water - Distilled
 Tap
 Sea

TABLE IV

**Results of Stress Corrosion Tests for
Type 419 in Various Media**

Applied stress - 100,000 lb/in.² Cracking time in hours

Media	Tempering Temperature				Reference	Type Loading
	315°C (600°F)	482°C (900°F)	538°C (1000°F)	598°C (1100°F)		
0.1 NH ₂ SO ₄ + 3 Mg As/1	0.66	0.08	0.66	NF	26	CD
18% HCl + 1% SeO ₂	-	-	1.4	NF	25	CD
	0.9	0.6	0.25	0.2	•	CL
½ HAc + 6 NaCl + H ₂ S	2.2	1.2	0.35	9.2	•	CL
½ HAc + H ₂ S	-	-	5.0	25.0	46	CD
	150	34.0	130.0	>1000	•	CL
3-5% NaCl Fog	>1000	-	-	-	33	CD
	>1900	144- 1200	264-NF	NF	26	CD
	-	-	-	1680	32	CL
	14,000†	2800	3400	-	18	CL
Marine Atmosphere	>5000	504	1000	>5000	•	CD
Industrial Atmosphere	>10,000†	3400†	9100	-	18	CL

• Armco Steel Corporation - Unpublished Data

† 145,000 lb/in.²

CL - Constant Load

CD - Constant Deflection

NF - No Failure

TABLE V

Stress Corrosion Resistance of 17-4 PH in Various Media

Applied stress - 100,000 lb/in.² Cracking time in days

Media	Aging Temperature			Reference
	482°C (900°F)	552°C (1025°F)	620°C (1150°F)	
18% HCl + 1% SeO ₂	0.5	0.04	>100	*
½ HAc + 6 NaCl + H ₂ S	0.17	0.05	0.15	*
½ HAc + H ₂ S	2-62	50 NF	50 NF	33
3-5% NaCl	42 NF	-	-	33
	14-50	-	75 NF	32
20% NaCl	42 NF	-	-	33
Marine Atmosphere	573 (-)	2400 NF ⁽²⁾	2400 NF ⁽³⁾	30 ²

* Armco Steel Corporation - Unpublished Data

NF - No Failure

(1) Applied stress 163,000 lb/in.²(2) Applied stress 140,000 lb/in.²(3) Applied stress 105,000 lb/in.²

TABLE VI

**Mechanical Properties and Stress Corrosion Resistance
17-4 PH and PH 13-8 Mo**

Solution treated and aged 593°C (1100°F)

<i>Mechanical Properties*</i>	<i>PH 13-8 Mo</i>	<i>17-4 PH</i>
Ultimate tensile strength, lb/in. ²	170,000	150,000
0.2% yield strength, lb/in. ²	150,000	135,000
% Elongation in 2 in.	16	17
% Reduction of area	50	58
Impact, Charpy V-notch, ft lb	100	45
<i>Stress Corrosion Tests*</i>		
½ Acetic Acid + 6% Salt + H ₂ S		
Applied stress 50,000 lb/in. ²		
Hours to failure	150	3
200°C (400°F) water **	> 2,000	< 1,000

* Armco Steel Corporation

** 17-4 PH stress - 138,000 lb/in.² - aged at 482°C (900°F)

PH 13-8 Mo stressed - 147,500 lb/in.² - aged at 510°C (950°F)

Cl - < 1 ppm O₂ - 4-5 ppm

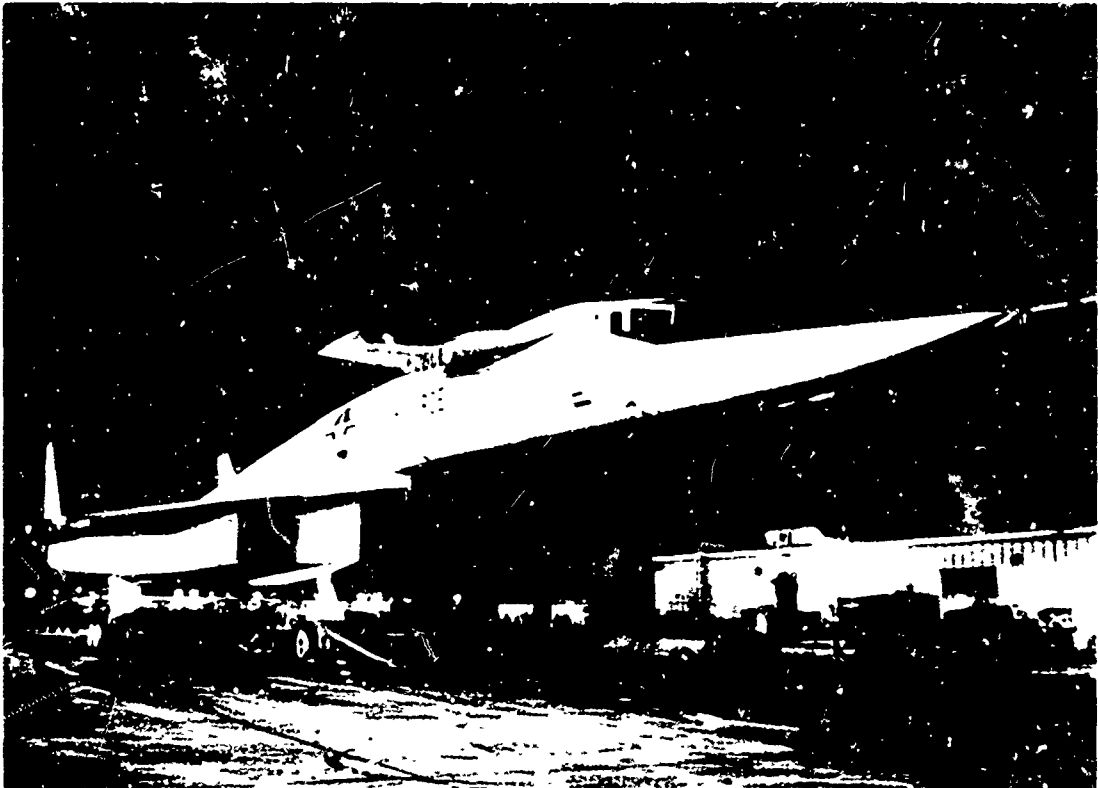


Fig.1 High strength stainless steel airplane. North American Aviation XB-70

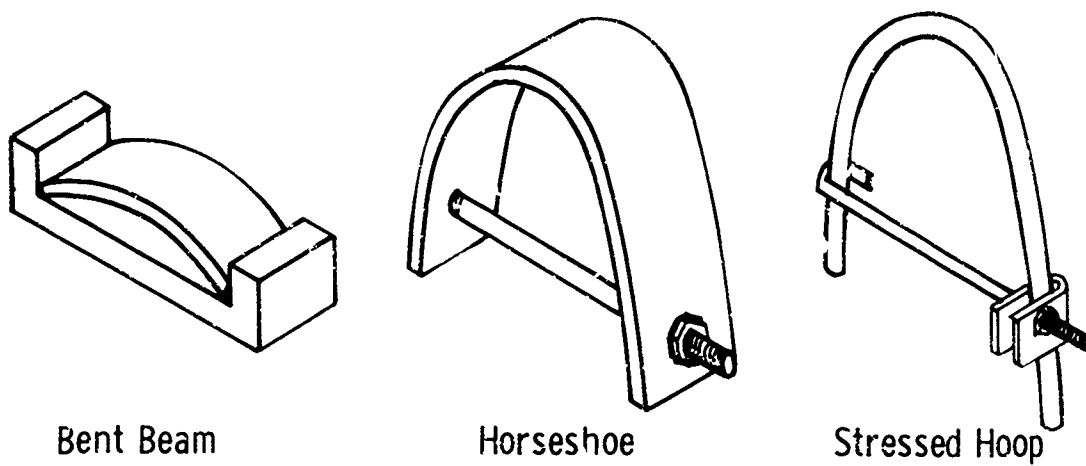


Fig.2 Stress corrosion test methods (constant deflection)

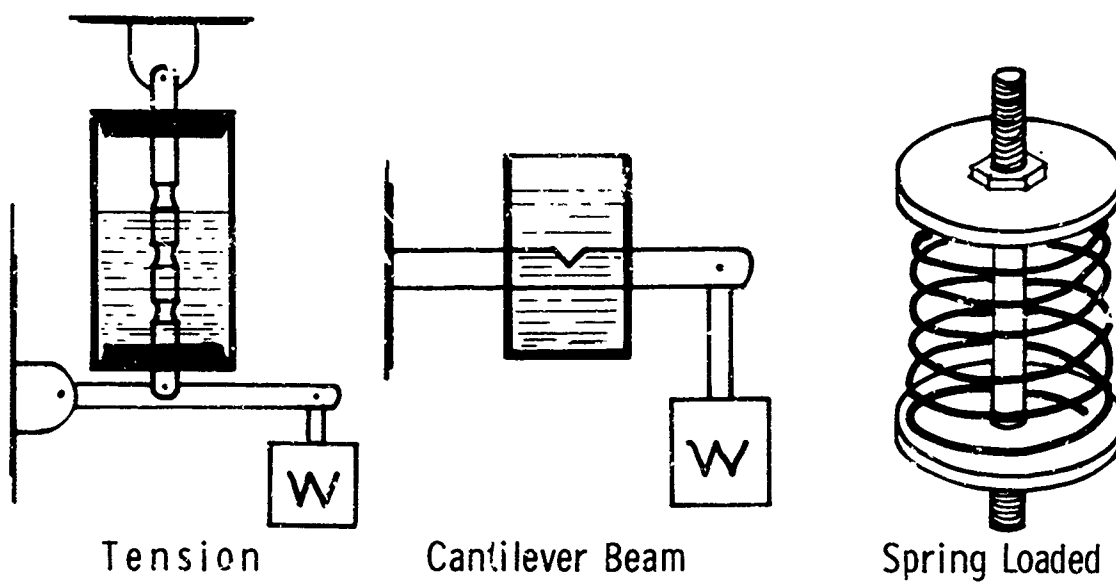


Fig.3 Stress corrosion test methods (constant load)

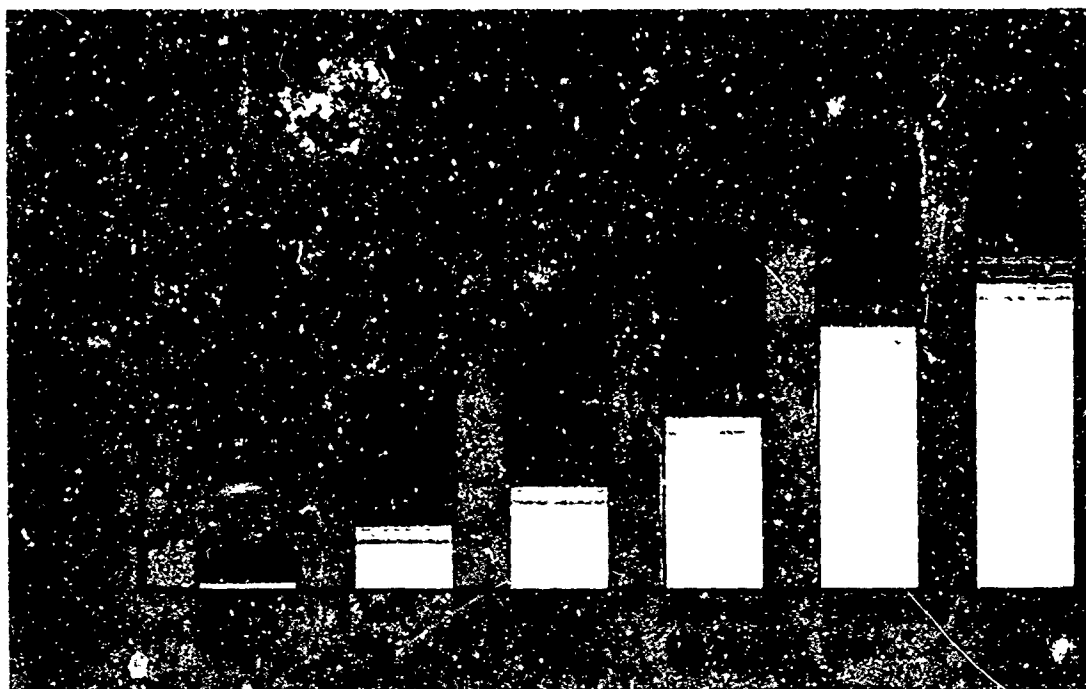


Fig. 4 Relative severity of various environments

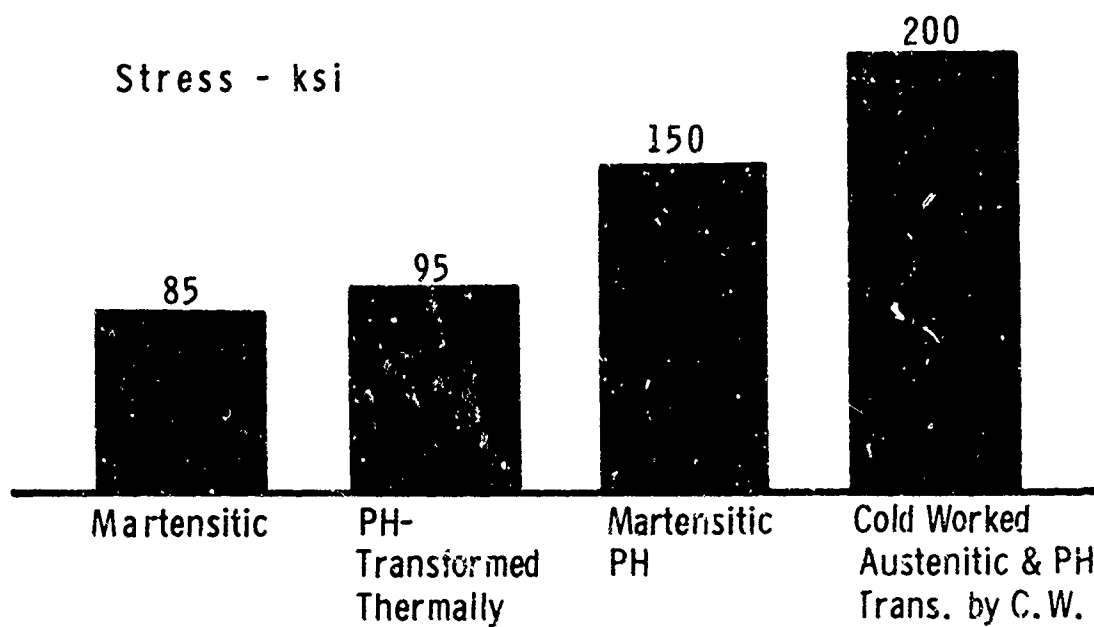


Fig. 5 Suggested applied safe stress for high strength stainless steels in marine atmosphere. (ksi = 1000 lb/in.²)

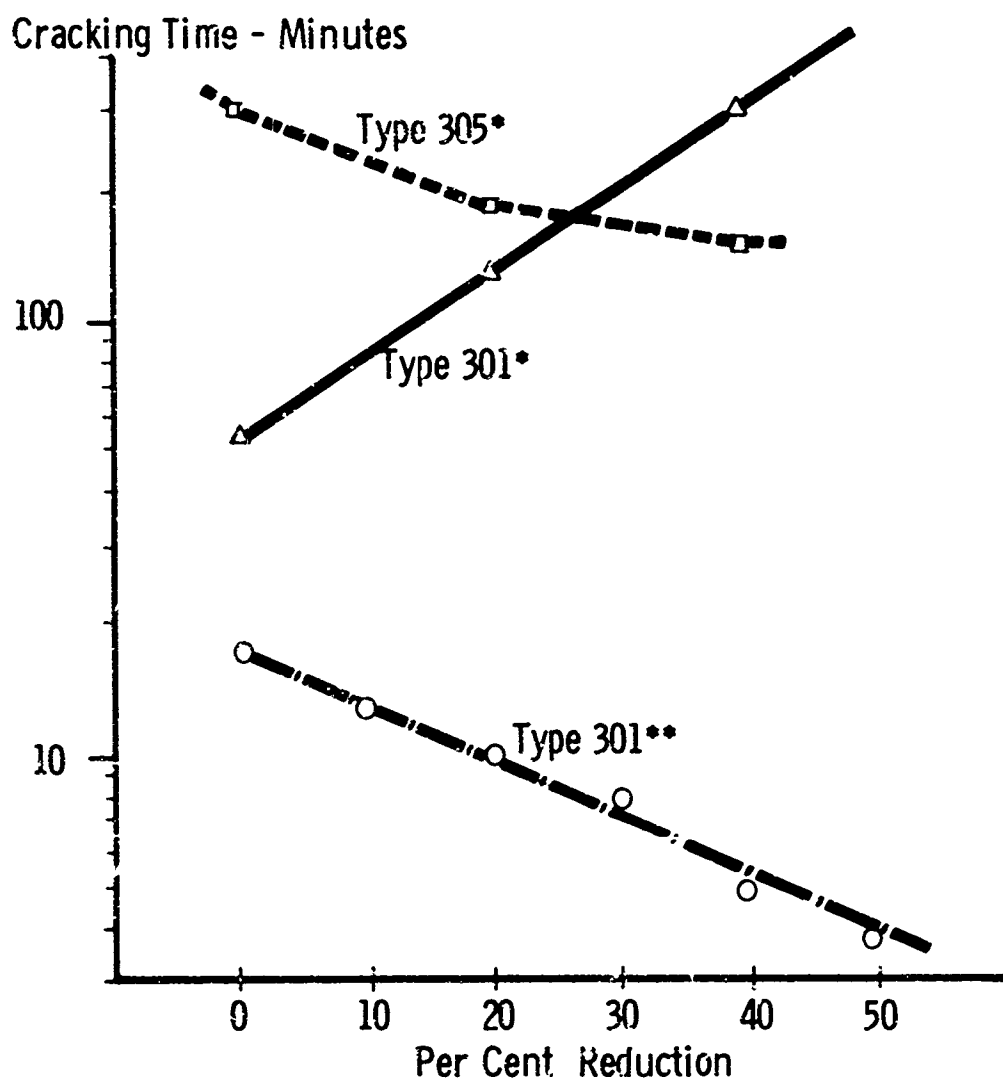


Fig. 6 Stress corrosion cracking time, cold worked austenitic alloys

* Unpublished data-Armco Steel Corp.

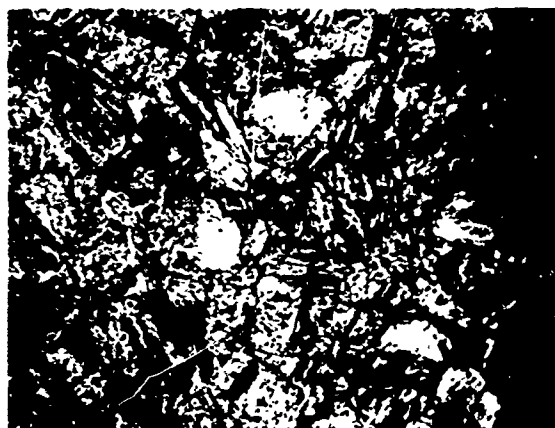
** Ref. 29



1/2% acetic acid, 6% salt,
hydrogen sulfide

100,000 lb/in.² 0.85 hours

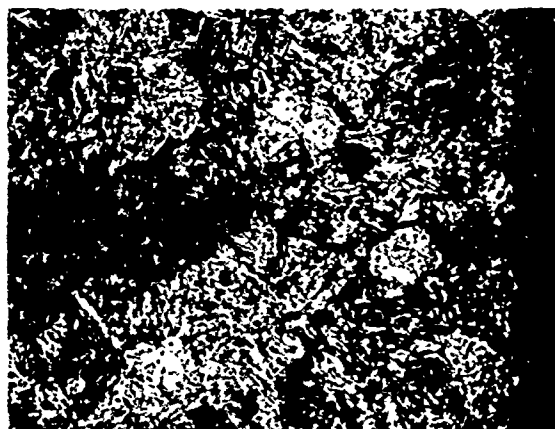
Transgranular Cracks



Boiling 42% magnesium chloride

100,000 lb/in.² 21.8 hours

Intergranular Cracks



Marine atmosphere, 80 ft from ocean

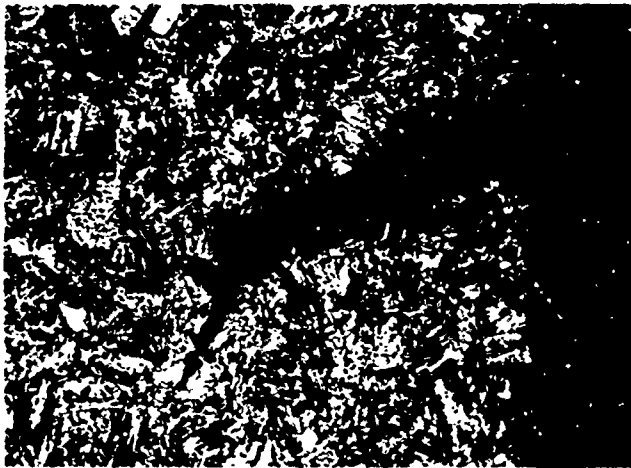
140,000 lb/in.² 504 hours

Intergranular Cracks

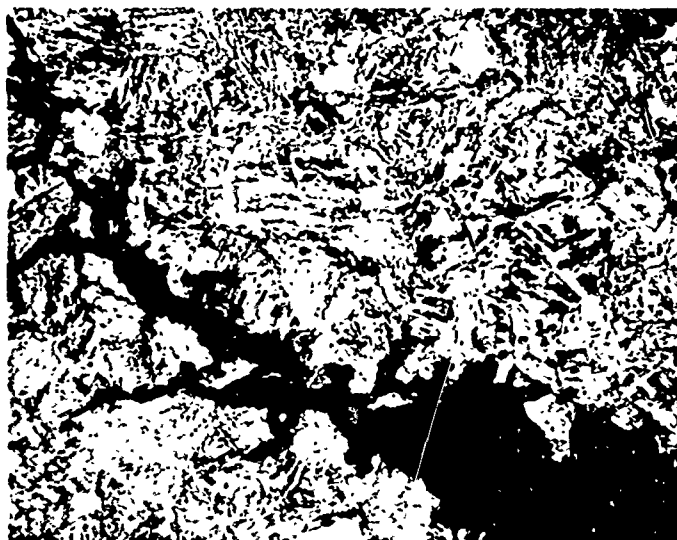
Fig.7 Stress corrosion cracks in Type 410 exposed to various media

Hardened and tempered at 482°C (900°F).
Magnification 250 ×

V-34



Crack perpendicular to applied stress



Intergranular crack perpendicular to fracture face

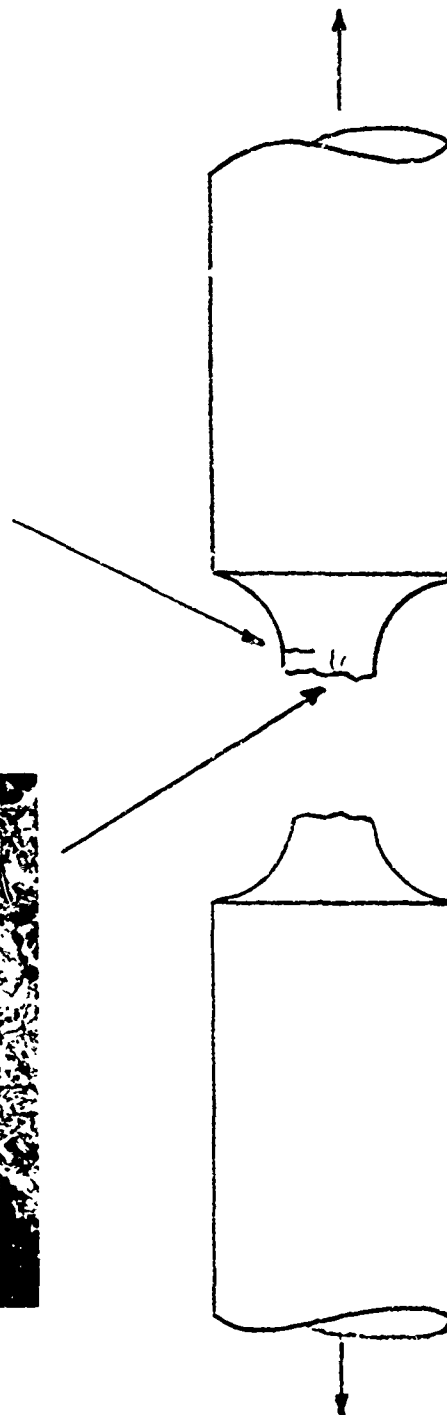


Fig. 8 Stress corrosion cracks in notched tensile specimen of Type 410
exposed to 18% HCl + 1% SeO₂

Hardened and tempered at 482°C (900°F)
Magnification 250 ×

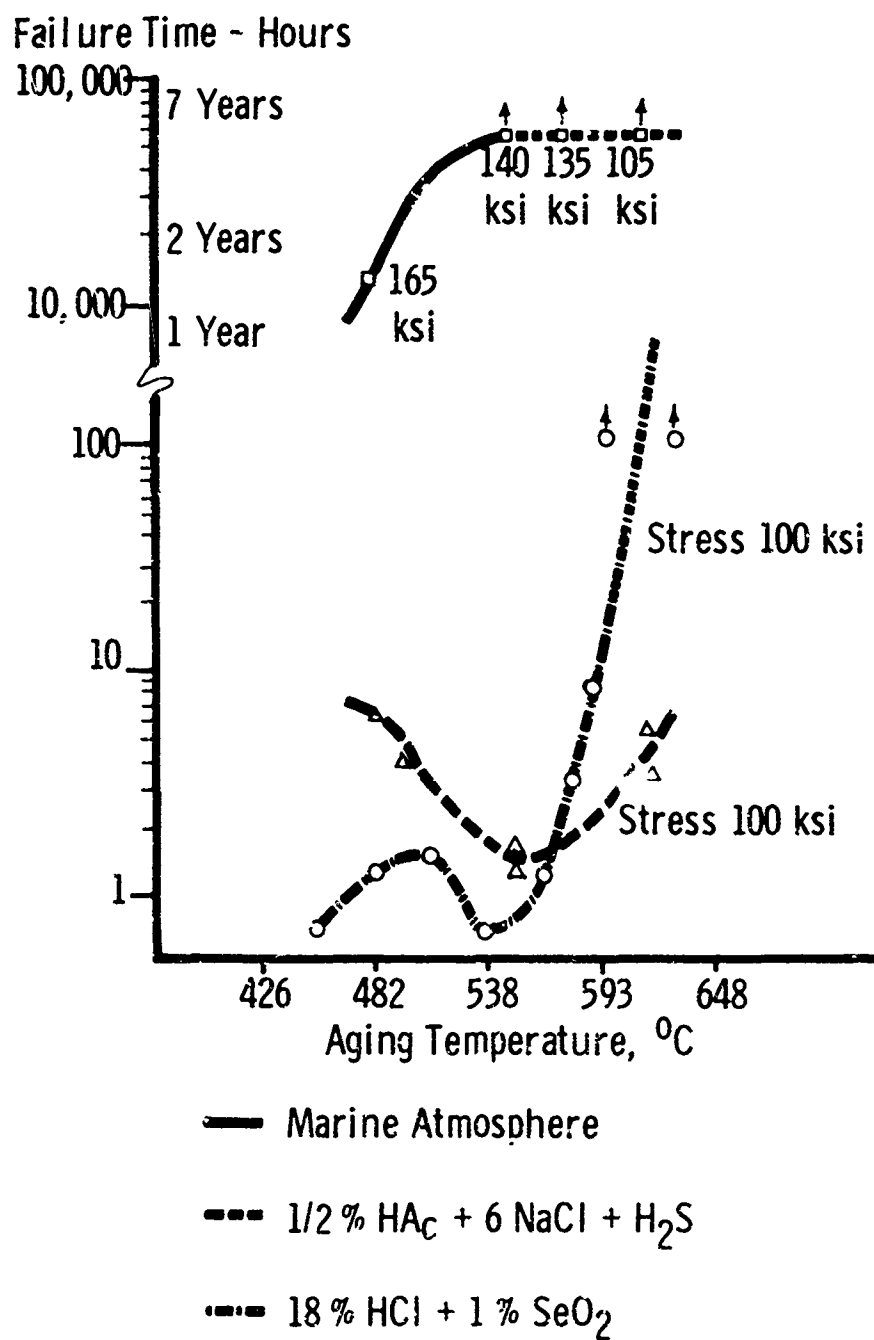


Fig.9 Effect of aging temperature on stress corrosion resistance of 17-4 PH in various media

DISCUSSION ON PAPER BY E.E.DENHARD, Jr

(i) Mechanism

Professor L.Graf referred to work he had carried out on 18Cr11Ni steel, of the homogeneous non-saturated type referred to in his comments on Professor Fontana's paper. Although the elements in solid solution gave increased reactivity at grain boundaries and at disturbed areas in the grain surfaces, and at regions in a state of deformation, it had been shown that the potential difference between flowing and non-flowing metal was insufficient to cause SCC. For SCC to occur, the crack walls must be polarised cathodically. Professor Graf described in detail experiments with a potentiostat on specimens static and under deformation which showed that the crack walls became cathodically polarised with passive films and that the cathodic reaction was the discharge of hydrogen. Polarisation of the whole specimen to negative potentials stopped SCC by activation of the crack walls.

Dr J.C.Scully made a comment from his own work on austenitic stainless steels in which he was seeking to distinguish between the role of anodic processes and the possible role of hydrogen. Thin foils had been prepared from type 304 specimens stress corroded in water plus a trace of chloride at 270°C. The crack passed through slip planes by plain anodic dissolution. No second phase was present. The effects of hydrogen charging in poisoned sulphuric acid were being studied; charging type 304 caused the formation of eta martensite, with attendant plastic strain and stacking fault ribbons. No phase change occurred with type 310 steels. After charging, the potential was lowered and the passive film removed. While the specimen was being removed from the acid, however, it repassivated, i.e. anodically polarised itself. During this repassivation severe dissolution occurred along slip planes giving an appearance similar to the stress corroded specimen. It was concluded that repassivation was an important phenomenon, and that a critical part of the SCC process was delay in repassivation at the crack tip.

Dr E.H.Phelps said Mr Denhard's paper emphasised the importance of relating test environment to service; any metal could be made to stress corrode if one tried hard enough. SCC in service was nearly always due to residual stresses which were higher than service stresses; it was better to temper at a higher temperature to reduce internal stresses, even though the applied load would then be a higher proportion of the tensile strength.

(ii) Metallurgy

Mr Waller asked what was the effect on resistance to SCC of transformation of unstable austenite to psi martensite, and a French delegate enquired the effect of small quantities of ferrite in types 410 and 431. Mr Denhard replied that resistance to SCC rose when austenite was transformed to psi martensite. Ferrite was helpful; SC cracks propagated through martensite and avoided ferrite in these and in austenitic alloys containing ferrite. But ferrite was harmful to transverse mechanical properties, and alloys were now being produced free from ferrite and untransformed austenite. Higher chromium contents increased resistance to SCC, so type 431 alloys were more resistant than type 410 at the same strength level.

(iii) Test methods.

On the question of test specimens, Mr Waller asked how one calculated the stresses in bent beam test specimens, and were these specimens not very sensitive to imperfections in the surface? Mr Denhard gave more details of preparation of test specimens. In tensile type bar specimens, notches of K1.3 were cut. The specimens were rough machined in the hot rolled condition, solution treated and aged or tempered, then given grit polish and, in the case of austenitic alloys, an electropolish. He agreed that surface imperfections had an effect on bent beam tests; specimens were ground, vapour blasted and handled with gloves. Stresses were calculated from bent beam formulae; the region of uniform stress on a 7 inch long specimen was about 5 inches. Reproducibility in tests was good, in spite of random pitting.

Dr Phelps added that his Company had made available methods for the exact calculation of stresses in bent beams. Stresses in outer fibres of specimens could be calculated to $\pm 5\%$ up to 75% of the yield strength. In further reply to Mr Waller, Mr Denhard explained that his stressed hoop and horseshoe specimens were bent to approximate shape, then heat treated and cleaned, and then bent further to introduce the required stresses. Strain gauges had been used to calibrate the jigs.

STRESS CORROSION OF TITANIUM ALLOYS

by

J. B. Cotton

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STRESS CORROSION OF TITANIUM ALLOYS

J. B. Cotton

SYNOPSIS

Although titanium and its alloys are resistant to corrosion in many media including aqueous solutions of chlorides, stress corrosion of some titanium alloys can take place in halide environments. The circumstances under which this occurs are summarised with particular reference to exposure in hot unstabilised chlorinated hydrocarbons, to hot dry sodium chloride and to aqueous saline solution at ambient temperature.

Cracking in a range of chlorinated hydrocarbons can be avoided by addition of suitable stabilisers and inhibitors to the degreasants, and conditions leading to use of safe degreasing systems are defined.

Where an aircraft component is in contact with wet salt this may evaporate at engine heat and could give rise to hot-salt stress corrosion. Although no example from service has yet been found, the effect can be produced in the laboratory and the results of a great deal of laboratory investigation and testing are summarised. The effect is found mainly in titanium alloys containing aluminium and sensitivity to cracking increases with aluminium content. Sensitive alloys can be rendered significantly less sensitive by additions of molybdenum and vanadium. The metallurgy and chemistry involved in cracking in hot salt is discussed together with possible protective measures.

Stress corrosion cracking of titanium alloys can also take place in salt water at ambient temperatures but the conditions under which this occurs involves a very high level of local stress. Again the effect has only been seen in the laboratory under conditions imposed by pre-fatigue cracking followed by cantilever stressing of the cracked region. The circumstances involved in this sort of situation are reviewed and discussed.

Finally, features common to cracking in all three environments are collated and discussed with respect to fundamental aspects of stress corrosion and of the direction in which remedies may be sought.

1. INTRODUCTION

Stress corrosion must surely be the most ubiquitous and insidious of all corrosion phenomena. In its ubiquity it is recognised in materials as widely separated as gold alloys and methyl methacrylate and anyone who has kept a favourite spun brass bowl for years, only to see it suddenly and spontaneously fall apart, can testify as to the insidious nature of the process.

The complexity of the problem is such that the only established features known with complete certainty to apply across the entire field of enquiry are the presence of stress and a fairly but not uniquely selective corrodent. As far as metallic materials are involved it seemed, until very recently, that one other certainty was that the phenomenon could only occur in alloys and not in really pure metals. There now seems to be some doubt even about this, since Pugh and Woodward have produced the effect in copper of 99.999% purity¹.

Against this background, and with an admitted ten years' hindsight, it was clearly a forlorn hope ever to imagine that titanium and its alloys or any other metal and its alloys, for that matter, could ever be completely immune to this catastrophic form of failure. Thus the best that can ever be expected from any metal being newly developed industrially is that its stress corrosion behaviour will be confined to environments well removed from those encountered in commerce and industry.

In its early days, titanium seemed to fulfil this requirement. The commercially pure metal was known to stress-crack in red fuming nitric acid and even in methanol but in any event it could not be safely used to contain red fuming nitric acid because of an explosive hazard, and there seemed little need to employ it for processes involving methanol. Provided temperatures are kept below about 250°F (121°C) the metal does not corrode in aqueous solutions of neutral halides and this has encouraged its successful use in a wide range of chemical plant applications involving this type of environment. Indeed, about 1952, Kiefer and Harple² exposed stressed titanium to sixteen different chloride solutions without obtaining any evidence of cracking. In 1955, however, G.W. Bauer³ reported surface cracking in a Ti-6Al-4V alloy during creep testing at 700°F (371°C), but this was at first attributed to surface oxidation and its recognition as true stress corrosion was delayed mainly by difficulties in reproducing the effect.

The full disappointing realisation that chlorine or chloride in some form could produce stress corrosion became only too apparent in 1957 when Meredith and Arter⁴ reported stress corrosion cracking of an Ti-5Al-2.5Sn alloy weldment exposed to chlorinated diphenyl at 707°F (375°C). Since about that time the witch-hunt has intensified and in 1967, with broomsticks moving into the supersonic region, titanium and its alloys have been undergoing an ordeal by fire and water probably unequalled in any other candidate metal used in aircraft.

There are, in fact, at least three environmental hazards that titanium may encounter in its journey from the billet through its working life in aircraft and they all involve chlorine or chloride in one form or another. It is in these environments, recreated in the laboratory, that titanium alloys are being subjected to stress conditions at least as severe and usually much more severe than anything they will have to endure in service. In the fabricating stage an aircraft component may well be lubricated or degreased with a chlorinated hydrocarbon in one form or another; it may literally acquire some of the human sweat normally metaphorically lavished upon it and the sweat will contain some salt and during its lifetime in an operating unit it may be baptised with salt from deiced runways or, if carrier-based, from sea water. At engine heat this leads to the third environment in the form of decomposing solid salt.

A great deal of investigation by several teams of investigators has been made into the cracking of titanium alloys in hot salt and an accelerating effort is being devoted

to behaviour in aqueous salt solutions, but the effect of decomposing chlorinated hydrocarbons upon titanium alloys has not been previously published in any detail. The objective of this paper is thus to remedy the situation in respect of chlorinated hydrocarbons, to summarise the available results of work with hot salt and aqueous salt solutions, to discuss possible mechanisms leading to failure in all three environments and to suggest directions in which remedies may be found.

2. STRESS CORROSION OF TITANIUM ALLOYS IN CHLORINATED HYDROCARBONS

The information that Ti-5Al-2%Sn had failed by stress corrosion in chlorinated diphenyl¹ was independently confirmed in the Research Department at Witton when stress corrosion was detected in a welded component fabricated from the same alloy, as it was being degreased in trichlorethylene vapour. To define the situation more closely an investigation was mounted in three directions.

- (i) To confirm that the effect could repeatedly be reproduced with the Ti-5Al-2%Sn alloy and to determine in which, from a range of chlorinated hydrocarbons, stress corrosion was likely to occur.
- (ii) To determine in which, from a range of commercial titanium alloys, the effect was likely to be found.
- (iii) To see whether appropriate additions to chlorinated hydrocarbons could ensure compatibility with titanium alloys and avoid stress corrosion.

2.1 Tests with Titanium-5% Aluminium-2% Tin Alloy and Chlorinated Hydrocarbons

Because it is known that, on prolonged exposure in the presence of some metals, the vapour of trichlorethylene C_2HCl_3 , can partially decompose to produce hydrochloric acid, it has long been customary to control acidity by the addition of a stabiliser such as triethylamine at a strength of about 0.02%.

This environment was employed in an attempt to crack machined cylindrical specimens of Ti-5Al-2%Sn alloy in straight tensile pull at 95% of the proof stress. None of these specimens fractured even after exposure for 850 hours. When, however, specimens were welded in the centre of the gauge length and stressed, they cracked within fifteen minutes (see Figure 1). Unwelded samples, heat-treated to simulate the welding-temperature cycle, did not crack and it was assumed that additional stresses introduced during welding influenced cracking behaviour.

Specimens were therefore cut from sheet and bent into a loop so that there was both plastic and elastic strain at the apex of the loop. These always cracked in the stated environment within thirty minutes (Fig. 2). The cracks were transgranular (see Figure 3).

Having established a condition in which cracking could be guaranteed, the bent loop system was used to obtain information upon the type of chlorinated hydrocarbon, vapour or liquid, in which cracking was likely to occur. The results, recorded in Table I, indicate that most chlorinated hydrocarbons, in the unstabilised form, are likely to give rise to cracking but there is evidence that this may be a function of temperature.

since there was no cracking in liquid trichlorethylene at 20°C nor in the vapour of chloroform at 61°C.

2.2 Tests with a Range of Commercial Titanium Alloys

Using unstabilised trichlorethylene vapour at a temperature of about 38°C, a wide range of titanium alloys, most of them developed for use in aircraft, were subjected to the form of cracking test previously described. Where, because of mechanical strength properties, it was not possible to bend the strip into a loop, bowed specimens were used (see Figure 4) and, to ensure that some specimens would be in the most susceptible condition, a transverse weld was made in the region of maximum stress with about half the specimens used.

For a degreasing bath, time of contact of metal with the degreasant is not normally longer than, say, half an hour, and a degreasing system can be deemed to be safe if cracking at the very high stresses employed does not occur within, say, a hundred hours.

From the results recorded in Table II, it may be seen that there was no cracking with commercially pure titanium, nor any titanium alloy that did not contain aluminium, and this was so even when the time of exposure was extended to three hundred and fifty hours. There is some evidence that the presence of a critical proportion of aluminium may be necessary before cracking takes place and that this may be of the order of 4 wt %. Thus there was no cracking with the titanium 2% aluminium 2% manganese alloy. The cracking tendency may, of course, be complicated by the presence of other elements, e.g. tin or zirconium, and by heat treatment or mechanical deformation, but more investigation is necessary before this aspect is completely defined.

2.3 Effect of Additions of Stabilisers and Deactivators to Chlorinated Hydrocarbons upon Stress Corrosion of Titanium Alloys

It seems very probable that the types of chemical reaction taking place during the stress corrosion of titanium alloys containing aluminium are very similar to those known to occur between the same chlorinated hydrocarbons and aluminium and it is appropriate to list these. The details of all the reactions are not known with complete certainty but they fall into three categories - an organic condensation reaction catalysed by the metal surface, during which hydrochloric acid is formed, an oxidation of the chlorinated hydrocarbon which could also produce hydrochloric acid and corrosive attack by the hydrochloric acid on the metal. During these reactions aluminium chloride is formed and this can also catalyse further decomposition of the chlorinated hydrocarbon.

In order to counter the total effect it is clearly appropriate to attempt to suppress all three types of reactions and this can be largely achieved by making appropriate additions to the chlorinated hydrocarbon. Thus as antioxidants, derivations of pyrrole (C_4H_5N) or a form of unsaturated hydrocarbon butylene (C_4H_6) is used; the last mentioned type of compound may also act as a metal deactivator, but some esters and ketones can also function in this way. Finally reagents such as aliphatic amines, e.g. triethylamine (C_2H_5)₃N, organic oxides, known as epoxides, and chlorinated esters are added to prevent the development of acidity - see the patent literature^{5,6,7}.

The beneficial effect of the additions designed to suppress all three types of reaction are evident when the stress corrosion test is repeated with trichlorethylene. Methyl chloroform is normally used cold, and does not produce cracking, but a stabiliser is usually added to make assurance doubly sure. Results of tests with stabilised and unstabilised degreasants are recorded for the Ti-5%Al-2½%Sn alloy in Table III.

Summarising the results of all this work, it can be seen that there is no evidence of stress corrosion when commercially pure titanium or titanium alloys not containing aluminium are exposed to hot chlorinated hydrocarbons. Where the aluminium content exceeds a critical amount, a stress corrosion hazard exists and this is accentuated at welds. Both plastic and elastic strain are a necessary pre-requisite for stress corrosion cracking in these alloys. The effect appears to be dependent, in part, upon the temperature of the degreasant, but for all practical degreasing purposes the hazard can be eliminated by suitably stabilising the degreasant and deactivating the metal surface.

3. HOT SALT CRACKING OF TITANIUM ALLOYS

Early attempts to reproduce the sort of surface cracking first reported by Bauer³ by finger printing titanium alloys and stressing them at elevated temperatures produced very mixed results⁸ and, for example, the cracking could not be produced by this means in the I.M.I. Research Department at Witton. When, however, wet sodium chloride is applied to certain types of titanium alloy specimens and allowed to dry and the specimen is then stressed in tensile pull at temperatures of the order of 600°F (316°C) to 900°F (480°C), cracking can be produced over a period of time, depending upon the level of stress. It can, for example, be as long as 30,000 hours with low stresses at 650°F (343°C) or in as short a time as 15 minutes when loaded under creep conditions at 900°F (482°C).

A great deal of research effort has been expended in attempts to define the conditions under which this effect occurs, in elucidating the mechanism, and in seeking a remedy. The complexity of the problem becomes apparent from the published record STP 397 of the thirteen papers presented at the Symposium on Stress Cracking of Titanium⁹ held under the aegis of ASTM at Seattle in October-November 1965. While, from these papers, there is a measure of agreement upon some important aspects there is discrepancy upon other issues.

For the purposes of this paper, an attempt will be made to summarise the situation as it appeared to be about mid-1966. It is convenient to do this by considering metallurgical aspects and chemical aspects separately.

3.1 Metallurgical Factors

A prime interest has clearly centred around alloy composition and, although by far the majority of investigators looked solely at titanium alloys containing aluminium, there is an unavoidable conclusion that, in titanium alloys containing aluminium, it is through aluminium that the effect operates, with tin having possibly a secondary adverse influence. Thus the most susceptible alloy appears to be Ti-5%Al-2½%Sn. There appears definite evidence that the higher the aluminium content the more susceptible the alloy, but any attempt to assign a limit to the maximum aluminium content is

difficult because of the influence of other elements added to maintain high mechanical properties. Commercially pure titanium appears to be immune and alloys not containing aluminium such as Ti-15%Mo, hot salt tested at I.M.I. Research Department, Witton, have not cracked. There is some evidence that, even when aluminium is as high as 8%, an alloy can be rendered less sensitive by additions of vanadium and molybdenum and possibly zirconium. More than one research team reports least sensitivity in Ti-6%Al-4%V but the alloy I.M.I. 679, containing 11Sn-2.25Al-5Zr-1Mo and 0.2Si, is considerably less sensitive than the Ti-6%Al-4%V (Ref.10). Lowering aluminium content to the order of 2% and adding 4% each of molybdenum and zirconium produces an alloy immune to cracking when tested at about 25% of the yield stress at 800°F (427°C) for 200 hours.

When cracking occurs it can be either intergranular or transgranular in habit and, in view of the fairly positive influence of aluminium in respect of cracking, it was to be expected that evidence of segregation in some form would be sought, either simply as ordering or even as precipitation in compound form. This is one of the aspects in which the evidence is confusing but, in spite of the contradictions produced in attempts at factual analyses of the metallurgical situation, the overall impression to be gained is that some concentration of aluminium has taken place in crack-sensitive regions, and it seems possible that if this is preceded or accompanied by one of the "protective" elements, e.g. vanadium or molybdenum, the sensitivity in that region is lessened. This situation with aluminium and desensitising elements as alloying additions to basic metals other than titanium is not unknown¹¹, for example with aluminium bronze.

The intergranular and transgranular habit of cracks appears to be related to the microstructure in that, for alpha alloys, cracking is usually intergranular and, for alpha-beta alloys, transgranular across the beta phase. Although, however, the pattern is fairly well established, it does not seem significantly to affect sensitivity to cracking. Thus Ti-6%Al-4V, an alpha-beta alloy, is rated by most investigators as good but it is inferior to largely alpha phased IMI 679, while Ti-5%Al-2%Sn, also an all alpha alloy, is one of the most sensitive. Where two phases exist evidence of the influence of the type of microstructure, e.g. presence of an acicular phase or of "basket weave" structure, is conflicting and no very positive trend has so far been shown to exist.

3.2 Mechanism of Failure

The chemistry of the corrosion process taking place when hot salt reacts with titanium is complex and there are discrepancies and contradictions between results obtained by various teams who have attempted to identify a specific corrosive agent. Some investigators find that natural sea salt, containing magnesium and traces of other halides as well as chloride, is more aggressive than pure sodium chloride, but the reverse has also been reported and the overall picture seems to be that differences arising from the source of chloride are not significant.

It seems to be logical to assume that sodium chloride in solid or molten form would have to react to produce some further aggressive radicle which could then selectively react to initiate a crack and then continue to provide the corrodent to propagate the cracking process.

One fairly clear feature emerging from this part of the work appears to be that both oxygen and water are necessary as well as salt. The reaction products that could

then be formed at elevated temperatures are gaseous chlorine, hydrochloric acid, hydrogen, titanium dichloride, aluminium chloride, caustic soda, titanium dioxide and sodium titanate, so that it is not surprising that discrepancies in detecting one or other of these have been reported. There is even argument as to whether the aggressive radicle is gaseous, solid or liquid.

Attempting to summarise this complex situation, and believing, from some of the available evidence, that this stress corrosion process is mainly electrochemical in character, the author of this paper believes that the aggressive radicle is liquid, but that this could include moist gaseous chlorine. A titanium alloy surface that has been fractured at elevated temperature is certainly very reactive to hot salt and, in the I.M.I. Research Department, Witton, newly fractured surfaces covered with a film of liquid have been literally seen to "fizz" and the gas evolved was identified as chlorine in so much as it bleached litmus.

Some modification of the electrochemical mechanism has been put forward by one or two investigators who believe that hydrogen plays a part in producing embrittlement. Hydrogen could, of course, be produced by reaction between titanium and hydrochloric acid: at elevated temperature it would diffuse and, if present in sufficient quantity, it would precipitate in alpha phased titanium as brittle acicular hydride. To the best of the author's knowledge, no one has produced evidence of hydride in a hot salt cracked specimen, but it could be argued that the hydride is too small to be seen at normal magnification. More factual evidence is therefore required to substantiate embrittlement by a hydriding mechanism.

3.3 Influence of Temperature

Whatever the chemistry, the cracking process is accelerated by raising the temperature but there is a lower limit below which the effect will not occur in a reasonable time and there is also probably an upper limit in which severe corrosion occurs without giving rise to cracking. These limits appear to vary according to the alloy; the lowest figure of 400°F (204°C) has been quoted¹² for Ti-8%Al-1%Mo-1%V stressed at 50 ksi* for 5000 hours while figures of 800°F (427°C) and 1100°F (593°C) have been quoted for various alloys as the upper limit, beyond which cracking does not occur¹³.

3.4 Influence of Stress

Cracking is, of course, dependant upon level of stress, but several workers have produced curves of stress against temperature indicating a threshold condition below which fracture does not occur in a reasonable time - say 100 hours. In one series of tests, limiting stresses at 800°F (427°C) appear to be of the order of 20 ksi for Ti-6%Al-4%V, 23 ksi for Ti-8%Al-1%Mo-1%V, and 40 ksi for IMI 679 (Ref.10).

3.5 Recommendations

Faced with all the conflicting evidence upon the causes of cracking, the user of titanium alloys could hardly be blamed for taking the philosophical view that the primary chemistry scarcely matters. In any event it is most unlikely that the chemical aspect could be controlled - as it can be with chlorinated hydrocarbons - although salt on runways could be inhibited - so that the remedy is much more likely to be found by

* ksi = 1000 lb/in².

control of the metallurgy of the alloying system. Some encouragement can be gleaned from the fact that no failure has yet been reported from service and a clue to the reason for this is found in reports from several contributors to STP 397, who have found that by cyclic temperature testing susceptibility to stress corrosion cracking is virtually eliminated. This is probably because any corrosion initiated at elevated temperature is stifled when the temperature is lowered and that while, upon reheating, corrosion may start again, it does so at a fresh site. This often applies to pitting corrosion in a variety of metals and could well happen in service, with titanium alloys.

Apart from modifying the metallurgy of the system by addition of desensitizing elements, it should be possible to protect the titanium by some form of surface treatment or coating. For the simplest surface treatments, e.g. shot-peening, or anodising, only marginal benefit is reported and it seems probable that more substantial, non-porous physical barriers will be necessary. Aluminium dip coatings and nickel plating are said to be effective. Flame sprayed zinc, although porous, showed evidence of being beneficial and this would appear to operate via an electrochemical mechanism.

To conclude the summary upon this field of enquiry it is pertinent to observe that, while it is unfortunate that hot salt stress cracking has proved to be specific for aluminium, the one element added for strength purposes to most titanium alloys used in aircraft, it is encouraging to suggest that suitable remedies, either in the form of further alloying elements or as coatings, may well become available before a serious practical hazard arises in service.

4. STRESS CORROSION IN SALT WATER AT AMBIENT TEMPERATURES

In any metal-corrodent system known to produce stress corrosion cracks, there is always a time delay between the first application of the tensile stress and the onset of cracking, and this induction period can vary from a few minutes to a matter of hours, days or even years, depending upon the alloy, surface treatment, etc. Furthermore with a smooth metal surface, i.e. a surface smooth by normal engineering standards, the site of initiation of a crack appears superficially, at least, to be a matter of chance.

The reasons for the variable induction period and for the random nature of the initiating site are largely unresolved and form the subject of much discussion that cannot appropriately be summarised here. When, therefore, investigators wished to observe directly the onset of cracking, it has long been customary to use a deliberate defect, using a machined notch, at which complex tensile stresses could concentrate to ensure that the crack would start within a selected region. The presence of the defect also often shortened the induction period. Clearly the degree of stress concentration achieved by this means will be related to the depth of mechanical defect and the contour at the tip. These parameters will inevitably vary from investigator to investigator and it is not surprising that wide discrepancies in results have been reported.

This form of test acquired a new aspect when B.F. Brown^{14,15} developed a modified form of stress corrosion test by sharpening the notch by producing a fatigue crack from the base of a machined notch and using this fine, searching crack as the stress raiser from which, under static tensile pull, a stress corrosion crack could propagate.

It is argued that this procedure completely eliminates the induction period normally involved before a stress corrosion crack initiates at a normal smooth surface. Additionally, however, it is claimed that stress at the root of this type of defect can be treated mathematically after the manner of defects used for investigation of fracture toughness.

In the operation of this test a pre-cracked rectangular specimen is fractured by cantilever loading, first in air and then at various lower loadings when immersed in the saline solution at room temperature. The breaking loads are treated by the Kies¹⁶ equation to provide a factor known as stress intensity, K , having the units $\text{ksi}\sqrt{\text{inches}}$. K is plotted against time until the falling curve becomes asymptotic or near asymptotic with time, and the threshold value of K_1 is known as $K_{1\text{SCC}}$, i.e. the limiting stress intensity for stress corrosion. In attempting to evaluate the relative susceptibility of a range of alloys, however, the important feature is the extent of the fall in K_1 between the air value and the $K_{1\text{SCC}}$ value.

Although pitting corrosion and crevice corrosion of titanium had been previously noted in dilute sodium chloride¹⁷, this was always at temperatures in excess of 248°F (120°C) and until the development of the Brown test there had been no evidence of stress corrosion of titanium and its alloys at ambient temperatures in neutral saline solutions.

Compared to investigation on hot salt cracking, only a limited amount of work has been reported for titanium alloys using this type of test. One comprehensive series of tests¹⁸ indicates that the trend closely follows that reported for hot salt cracking in that titanium alloys containing aluminium are sensitive but that sensitivity could be eliminated by an addition of molybdenum or vanadium. There are, however, discrepancies between this work and results reported by another investigator who finds that, in certain sheet thicknesses, Ti-6%Al-4%V and Ti-8%Al-1%Mo-1%V are sensitive. There is even some discrepancy in behaviour of commercially pure titanium. One further additional piece of information available from published work on cracking in sea water is that Ti-8%Mn is sensitive to the effect, in addition to Ti-Al alloys.

Microstructure appears to exert more influence than it does in hot salt cracking and structures having fine distributions of alpha appear to be less sensitive than alpha structures or coarse alpha-beta structures; hence heat treatment can be expected to exert some effect on the result. Crack habit seems to be angular but transgranular in both alpha and beta phases.

The validity of the Brown test and its relation to any service failures that may eventually be encountered is likely to be vigorously debated. The test is fairly subjective in that a fatigue crack has to be stopped within certain limits, and results are certainly influenced by the size and form of test piece used and the rate of loading. To obtain useful results the pre-cracked specimen has to rupture quickly once cracking recommences under static loading and the fracture is then deemed to be "brittle". Indeed, there are some grounds for calling the effect "wet fracture toughness" rather than stress corrosion, but the fact that a corrodent such as sea water causes a significant lowering of the K_1 value when compared to the value obtained with distilled water is inescapable. The form of test-piece is important and, for example, for a rectangular bar in Ti-6%Al-4%V measuring 6 in. x 1 in. x 0.4 in., it is essential to machine side notches, in line with the primary notch, to ensure that "brittle" fracture

will occur. Even with this precaution it is necessary to repeat the test several times at each K_I loading and to average the results, to obtain each point in the curve with any precision.

The strong arguments in favour of the Brown test are that it may give to the design engineer an indication of the depth of mechanical defect from which a crack will or will not propagate and that any material giving favourable results in the test will be safer than one giving less favourable results.

Against this the view has to be recorded that, in practice, natural defects, not necessarily visible at normal magnification, are sometimes more potent in initiating cracks than mechanical defects and the test does not take these into account. There is also evidence that intermittent imposition of static stress is far less dangerous than continuous application, in that crack initiation may stifle and not re-start in the same place; even the tips of fatigue cracks have been reported to be insensitive to initiation of stress corrosion. Results of the Brown test may well therefore place an unrealistic restriction upon the selection of materials, particularly when no definite line can be drawn between apparently susceptible and non-susceptible materials.

5. DISCUSSION

The stress corrosion tendency of titanium alloys in the three environments, i.e. chlorinated hydrocarbons, hot dry salt, and aqueous salt at ambient temperature, can perhaps best be discussed by considering initiation and propagation of cracks separately.

From the haphazard nature of initiation, it seems very probable that the process requires the presence of active submicroscopic sites at the surface. Various reasons have been put forward for the existence of such sites; emergence of slip planes, pile up of planar arrays of dislocations at emergent barriers, such as stacking faults, the microscopic precipitation of hydrides and the lowering of surface energy locally. It is very probable that activity at a particular place is related to the degree of imposed strain. The fact that stress corrosion occurs virtually solely in alloys (even very dilute alloys), and not in pure metals, gives rise to the suggestion that there is diffusion of a corrosion-sensitive solute element to the sensitive site and that there is a connected path into the body of the metal. Since the metal is usually covered with protective film, coincidence is probably needed between some sort of defect in the film and in the metal surface proper. Specificity is also required in the corrodent and it may even be that a particular corrodent is specific only in certain concentrations. The necessity for coincidence in all these parameters would account for the haphazard nature of initiation.

Many of the features thrown up in this review of the large amount of reported work on stress corrosion of titanium alloys fit well into this broad picture. In all three environments and circumstances that result in cracking there seems to be a clear connection with the presence of aluminium, although diffusion of aluminium to particular sites has not been categorically proved. Assuming that attack by hot salt increases with increasing temperature, there is evidence of specificity within that particular environment, since one author in STP 397 reports an upper temperature limit at which hot salt cracking is replaced by more general corrosion¹³. This situation, where a critical concentration for cracking can be exceeded, is known in other metal systems, e.g. brass and sulphur dioxide and brass and ammonia.

Where the aggressive quality in the corrodent can be controlled, this will remedy the situation and the results of the work with chlorinated hydrocarbons demonstrates this.

To some extent surface sensitivity can be controlled mechanically, e.g. by shot-peening, but, of course, the effect of this can be nullified by high stresses imposed in service. Some control of surface activity could probably be achieved by modification of surface potential electrochemically, and this may well have been achieved by the good preliminary results reported in hot salt exposure for zinc coatings, even though these were porous¹⁹. Impervious coatings, e.g. nickel, will isolate the titanium alloy surface from the corrodent and, provided they have the necessary abrasion oxidation and corrosion resistance, these would provide an obvious remedy.

In the Brown test, the incidence of natural stress raisers at the surface is avoided, but here it could be argued that the metallurgically disturbed zone in advance of the fatigue crack creates its own local sensitivity.

When the crack propagates from the region of initiation into the metal, it is a moot point whether it follows an existing active path or whether an advancing sensitive zone precedes the growing tip of the crack. Evidence from transmission electron microscopy produced by Nutting and others suggests that planar arrays of dislocations piling up at stacking faults, slip planes and even grain boundaries constitute a pre-existing path and there has been argument as to whether there is diffusion of a solute element to such sites. The parallel experience, upon reactivity of aluminium alloys and titanium alloys containing aluminium when exposed to chlorinated hydrocarbons, might be held to support diffusion of aluminium in the titanium alloys and its preferential reactivity or dissolution in all the environments.

The influence of molybdenum and vanadium in countering sensitivity to stress corrosion seems to be fairly positive. Presumably these elements could function in either blocking off sensitive zones or by affecting the physical metallurgy, e.g. altering the stacking fault energy and the distribution of dislocations. One of the authors in STP 387 does in fact produce evidence obtained by micro-probe analysis indicating some segregation of molybdenum, vanadium and aluminium, but more evidence would be required before there is proof that the cracking could be avoided by control of diffusion or segregation of aluminium. In the stress corrosion field in general there is mounting evidence that, if it were possible to control the dislocation distribution to produce tangles, instead of planar arrays, this would go a long way towards alleviating this hazard. It should be noted, however, that there are systems having planar arrays that do not stress-corrode.

This physical metallurgy approach is an aspect that should be explored in still more detail by further use of high power transmission microscopy and modern physical methods of analysis. Such investigation might also produce explanations for the discrepancies thrown up by the various heat treatments.

The majority of investigators clearly believe that actual propagation of the cracks proceeds by an electrochemical dissolution, but one school of thought suggests that hydrogen plays an important part and that part of the cracking process could be true brittle fracture. If hydrogen is generated at the root of a crack and diffuses into the metal in sufficient quantity, it could obviously produce brittle hydride. The

extent to which it would do this would depend upon the micro-structure and the proportion of alpha to beta. Hydrogen is much more soluble in the beta phase than it is in the alpha and, if hydrogen were a significant factor, it would be expected that alpha alloys would be more susceptible than beta or alpha-beta. The evidence here is conflicting for hot salt exposure, but in salt water alpha alloys appear to be more prone, if sufficiently stressed.

It is doubtful whether precipitated hydride has ever been recognised in these stress-corroded alloys at normal optical magnifications, but Scully and Sanderson²⁰ have reported the presence of hydride at very high magnification by transmission microscopy. The material was thin foil Ti-5%Al-2%Sn which had been thinned by chemical and electropolishing and then stress cracked in 3% sodium chloride without notching. No cracking was observed with unpolished material and it is probable that the hydride resulted from the polishing reaction. Here again more evidence is required before hydrogen can be deemed to play a significant part in the initiation and propagation of stress corrosion cracks in these alloys.

6. CONCLUSIONS

1. Titanium alloys containing aluminium are susceptible to stress corrosion in some unstabilised chlorinated hydrocarbons and in hot salt, provided sufficiently high stresses are imposed.
2. In titanium alloys containing aluminium, a fatigue crack can be propagated by static stress in salt water at ambient temperature, again provided the applied stress is sufficiently high.
3. In all three media there are threshold stresses below which the effect will not occur.
4. The stress corrosion effect is promoted by the presence of aluminium and suppressed by the presence of certain other elements, e.g. molybdenum and vanadium.
5. In certain circumstances the stress corrosion can be suppressed by inhibiting or stabilising the corrodent, e.g. trichlorethylene.
6. The operating mechanism has not been fully elucidated, but the parallel effects observed in all three environments suggest there is a common origin. It is probable that the actual cracking proceeds by an electrochemical mechanism but hydrogen may play some part.
7. The remedies are likely to lie in some form of modification to the metallurgical structure but, provided it is acceptable from other aspects, a surface coating might provide an answer, and there are some circumstances when modification of the corrodent can be employed.

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TABLE I

Type of Chlorinated Hydrocarbon (unstabilised)	Temperature	Effect on Loop Specimens of Ti-5%Al-2%Sn (100 hour test)
Trichlorethylene (C_2HCl_3)		
Vapour	88°C	cracked
Liquid	20°C	not cracked
Carbon Tetrachloride (CCl_4)		
Vapour	76.7°C	cracked
Perchloroethylene (C_2Cl_4)	109°C	cracked
Chloroform ($CHCl_3$)		
Vapour	61°C	not cracked
Methyl Chloroform (CH_3CCl_3)	100°C	cracked
	20°C	not cracked
Orthodichlorobenzene ($C_6H_4Cl_2$)	179°C	cracked

TABLE II

Susceptibility of Titanium Alloys to Stress Corrosion Cracking in Unstabilised Trichlorethylene. Total Testing Time 100 hours.

Titanium Alloy	No. of Specimens Tested ^(a)	No. of Specimens Cracked
Commercially pure Ti	20	0
Ti-5%Al-2%Sn	40	40
Ti-4%Al-4%Mn	8	8
Ti-2%Al-2%Mn	6	0
Ti-6%Al-4%V	20	7 ^(b)
Ti-2%Cu	20	0
Ti-0.2%Pd	20	0
Ti-15%Mo	20	0

(a) Approximately half the specimens in each material were welded.

(b) Only welded specimens cracked.

TABLE III

Comparative Stress Corrosion Results Obtained With
Ti-5%Al-2%Sn Alloy Exposed to Unstabilised and
Stabilised Trichlorethylene and Methyl Chloroform.

	<i>Trichlorethylene</i>		<i>Methyl Chloroform Stabilised</i>
	<i>Unstabilised</i>	<i>Stabilised</i>	
No. of specimens tested	40	89	20
No. of specimens cracked	40 ^(a)	7 ^(b)	0

(a) All specimens cracked in a time of between $\frac{1}{2}$ hour and 22 hours.

(b) Only 7 out of 40 welded specimens cracked and none cracked before 19 hours, while some cracked only after 350 hours.

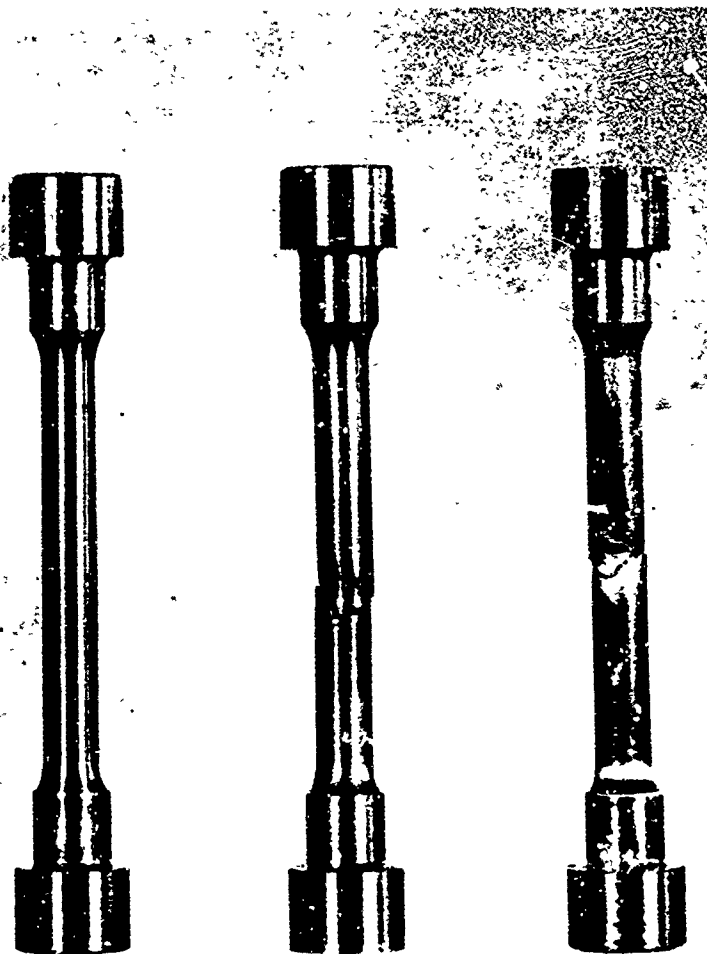


Fig.1 Specimens of Ti-5Al-2.5Sn stressed and exposed to unstabilised trichlorethylene vapour

Left - Specimen unwelded but heat treated to simulate welding cycle. Unbroken after 850 hours

Centre - Specimens welded in gauge length; fractured after 15 minutes and 55 minutes



Fig.2 Unwelded Ti-5%Al-2%Sn exposed to boiling, unstabilised trichlorethylene cracked in 30 minutes ($\times 6$)



Fig.3 Transgranular nature of cracks in stressed Ti-5%Al-2%Sn exposed to unstabilised trichlorethylene ($\times 150$)

VI-20

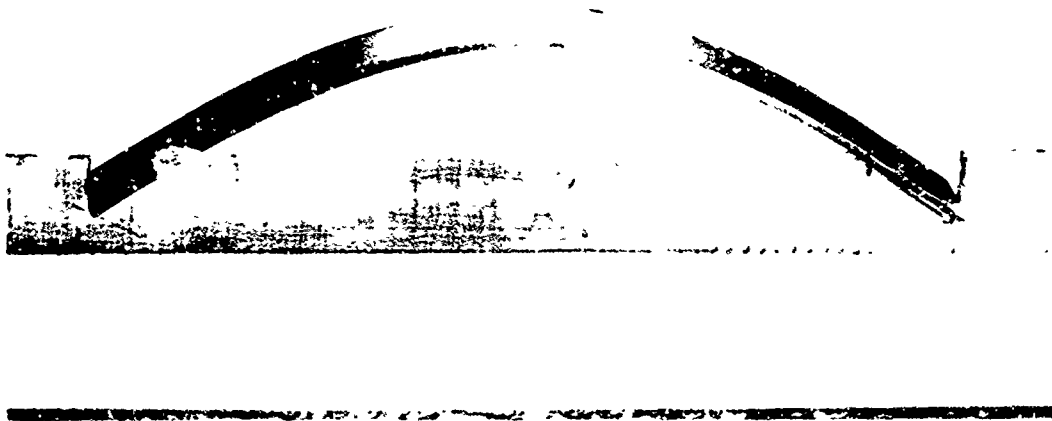


Fig. 4 Alternative method of stressing specimens for stress corrosion test ($\times 1\frac{1}{2}$)

DISCUSSION ON PAPER BY J. B. COTTON

Three speakers, Mr W.W.Minkler, Mr W.L.Williams and Professor H.U.Zwicker, made comments at length, and these were followed by a general discussion.

Mr Minkler said that a reading of recent technical literature might suggest that titanium parts in aircraft were failing by SCC with alarming frequency; in fact the situation was not nearly so bad. The following eight instances were, Mr Minkler believed, the only documented failures in ten years.

Aerospace Hardware Failures due to Stress Corrosion 1957-1966

<i>Alloy</i>	<i>Item</i>	<i>Media and Temperature</i>
Ti-5Al-2.5Sn	Missile Tank	Chlorinated Diphenyl, 375°C
Ti-6Al-4V (STA)	LEM Oxidizer Tank	Nitrogen Tetroxide, 40°C
Ti-6Al-4V (STA)	Apollo Tankage	Methyl Alcohol, 21°C
Ti-6Al-4V (STA)	Minuteman Case	Chlorides, 816°C
Ti-7Al-1Mo	Compressor Disk	Silver + Chloride, 482°C
Ti-8Al-1Mo-1V	Compressor Blade	Chloride, 482°C
Ti-4Al-4Mn	Compressor Disk	Cadmium, 303°C
Ti-5Al-2.5Sn	Compressor Case Weldments	Chlorides, 816°C

Most of these instances were easily cured:-

Nitrogen tetroxide, increase water content and reduce NO₂ content.

Methyl alcohol, increase water content to above 1%.

Chloride attack, avoid or remove chlorinated cutting fluids or chloride containing solvents before stress relieving or hot forming.

Cadmium, avoid contact with cadmium at service temperatures above 149°C.

Silver chloride, avoid the use of silver on wheel-spacer fasteners. Any one of these failures could have been predicted from a simple test using a notched beam bent beyond the yield stress.

Much laboratory work had shown that hot salt SCC could occur at temperatures as low as 260°C; nevertheless no failures had been met in engine parts operating in a marine environment at temperatures and stresses which cause consistent failure in laboratory tests. It was not clear why the laboratory test gave such pessimistic results; in service, parts operated in moving air, possibly damper than in the laboratory, and stress and temperature were intermittent, and perhaps one of these differences caused the discrepancy.

A similar discrepancy between test and service existed with regard to salt water environments. The two most common alloys used in aircraft had been Ti-5Al-2.5Sn and Ti-8Mn. The threshold stresses for failure of centre fatigue cracked specimens were reduced by 3.5% sodium chloride solution from the value in air of 106 ksi to 35 ksi for the 5Al-2.5Sn alloy, and from 110 ksi to 27 ksi for the 8Mn alloy. Despite these alarming figures, no problem had been reported from service.

Although no problems had arisen in service from hot salt corrosion or loss of fracture toughness in aqueous chloride solutions, choice and treatment of alloys were influenced by the results of laboratory tests. Alloys with SCC properties poorer than Ti-6Al-4V or Ti-8Mn-1Mo-1V would not be used unless there were some overriding advantage. A hot salt test had been included in specification AMS4910C for Ti-5Al-2%Sn. Hot working and heat treatment cycles were modified to give greater resistance to SCC. Fear of SCC sometimes led to unnecessary sacrifice of mechanical properties or density.

Much fundamental work on mechanisms was in hand, and a study was being made of the actual salt exposure conditions to which engines and airframes were exposed in service.

Mr Williams quoted work by I.R. Lane in his laboratory which showed that resistance to SCC depended not only on nominal composition but also on exact composition, mill processing history and heat treatment. In alloys containing aluminium, SCC properties depended on the amount of Ti_3Al present, its distribution and the magnitude of coherency strains caused by it, all of which were affected by heat treatment. Lane had carried out tests on precracked cantilever beams in air and in seawater on Ti-7Al-2Nb-1Ta and had interpreted the results in terms of recently published work by F. Crossley on the Ti-Al phase diagram from which it had been concluded that the Ti_3Al field extended further into the Ti rich end of the diagram than had been supposed (4 wt % as against 7.5 wt %), and that the partition of the aluminium between alpha and beta phases due to thermal history in the alpha-beta field was difficult to erase by subsequent thermal treatment below the alpha-beta field; both conclusions led to the belief that Ti_3Al was more common in Ti-Al alloys than had been supposed.

Lane found that seawater reduced the strength of the Ti-7.2.1 alloy delivered from the mill, to 45% of the air strength. Water quenching from a temperature above the alpha- Ti_3Al field, however, gave almost complete immunity to SCC, but ageing at 593°C, or slow cooling from above the alpha- Ti_3Al field, caused return of sensitivity to SCC due to the rapidity of formation of Ti_3Al . Furthermore, the partition of aluminium during holding within the alpha-beta field depended on the exact temperature of holding; less susceptibility to SCC was observed after holding at a temperature near the beta transus, for this gave a low-aluminium matrix and a smaller amount of material enriched with aluminium.

Further work by Crossley, as yet unpublished, dealt with the effects of third elements on the Ti-Al system. It was concluded that (i) ternary additions had an effect on the extent of primary alpha in Ti-Al-X alloys; tin increased the range of solubility, while oxygen, Zr, Nb, Mo and V decreased the solubility in the 700-800°C range, (ii) below 700°C, Mo and V appeared to increase the amount of Al needed to produce Ti_3Al , (iii) precipitation of Ti_3Al in Al binary alloys and in ternary alloys containing oxygen and Zr took place preferentially at grain boundaries, whereas in ternary alloys containing isomorphous beta stabilisers, there was no evidence of preferential precipitation at grain boundaries, and (iv) Zr, Nb, Mo and V make the precipitation of Ti_3Al more sluggish.

The above conclusions explained the excellent behaviour of the alloy modified by decreasing the aluminium content from 7% to 6%, and adding 0.8% Mo. The new alloy, Ti-6.2.1Mo showed no susceptibility to SCC in seawater after normal mill processing, after ageing at 593°C, and after welding. Furthermore, the corrosion fatigue strength in seawater was the same as in air, whereas that of the Ti-7.2.1 alloy was reduced, and the rate of propagation of a corrosion fatigue crack in the low cycle range was an order of magnitude less than that of Ti-7.2.1.

Professor Zwicker spoke of stress cracking at elevated temperatures in relation to composition and metallurgical condition. He pointed out that cracks formed on titanium alloys during creep tests at temperatures in the range 450 to 550°C in air without salt. In annealed alloys a few cracks formed and propagated along the alpha phase at grain boundaries to give a brittle fracture, for example Ti-6Al-4V extruded and annealed for 2 hours at 700°C and tested at 450°C under a stress of 47.5 kp/mm² (30.2 tons/in²) started to crack after 760 hours when the elongation was 8%. Alloy Ti-9Al-3V failed similarly with even less elongation. If, however, the grain boundaries were broken by cold working, cracking occurred only as many non-propagating surface cracks, and final failure was ductile. The shape of these non-propagating cracks depended on the composition, being wave-like in Ti-6Al-4V and straight in Ti-9Al-3V. The benefit of cold working in these creep tests seemed analogous to that of shot-peening in preventing the hot-salt cracking of Ti-8Al-1Mo-1V alloy.

Following reports that the metal at the surface of cracks formed during hot salt stress corrosion tests was enriched in alloying elements, in Al and Mo in the Ti-8Al-1Mo-1V alloy and in Al in the Ti-6Al-4V alloy, Professor Zwicker's laboratory had investigated the segregation of aluminium in the surfaces of a range of Ti-Al-X alloys heated to 550 to 600°C for 100-170 hours.

Microprobe analysis showed that alloys Ti-5Al-2%Sn, 6Al-4V, 7Al-4Mo, and 9Al-3V became enriched in aluminium in the surface, to the extent of 28% wt in the 9Al-3V alloy, the maximum solubility in the ordered hexagonal alpha phase. This enrichment led to susceptibility to cracking and to SCC. In the Ti-3Al-16V alloy, on the other hand, aluminium was depleted at the surface but in the oxide layer it was enriched and also in the alpha phase of the grain boundaries. It was concluded that aluminium diffused mainly along the grain boundaries to the surface and into the oxide layer, which, on this alloy, grew rapidly.

The diffusion of aluminium in the alpha plates along grain boundaries in the alpha-beta alloys explained the susceptibility of the boundaries to cracking as found in annealed alloys. This effect, and the surface cracking in cold-worked alloys, might be much accelerated by salt attack. It was concluded that alloys low in aluminium (< 4%) should be sought, with creep strength imparted by Zr, Mo etc.

Dr J.C. Scully spoke again of his ideas that SCC occurred when the passive film was broken and did not reform quickly. It was difficult to start cracks in titanium even by straining it in acidified sea water. To overcome the very rapid repassivation, fresh surfaces must be created faster than passivation took place. This could be done if a hydride film, formed by hydrogenation, were ruptured by straining in seawater. Alternatively, if an untreated strip were strained very rapidly in seawater, hydride formed and cracking started. He visualised a continuous formation of hydride at the crack tip; precracking was not essential. The hydride phase was very small; fractographs of specimens strained in air, water, or methanol revealed that hydrides of size < 0.1 micron formed on slip planes within seconds, causing transgranular brittle fracture in seawater.

Aluminium raised the ratio c/a of titanium, and thus increased the chance of forming hydride; it also reduced the readiness of titanium to repassivate. In the Ti-5Al-2%Sn alloy the grain boundaries were active; in this alloy rapid transgranular SCC could occur due to formation of hydride, and slower intergranular failure.

Mr Waller asked whether Mr Cotton's specimens for stress corrosion tests in chlorinated hydrocarbon solvents and salt solution had been passivated. In the USA passivation in mixed acids was always applied; passivation affected the SCC properties of stainless steels. Mr Cotton replied yes, in a nitric-hydrofluoric acid pickle which gave a passivated surface. Referring to Mr Minkler's instances of failure, he said he had not covered cracking in methanol in his paper, as he thought it irrelevant to aircraft. If the methanol were redistilled to very high purity, he believed it would not cause SCC. Mr Waller then referred to Dr Scully's hydrides and asked, what about dissolved interstitial hydrogen? Dr Scully replied that the hydride precipitate was interstitial. In his work on thin films, the metal was saturated with hydrogen as well as containing precipitate. Aluminium increased the solubility of hydrogen and also increased the size of the hydride precipitate. Dr Phelps supported Dr Scully's ideas on the importance of the rate of repassivation. In precracked bent beam tests on Ti-7Al-2Nb-1Ta in salt water, the results depended on whether the salt water was added before or after the load was applied. If the specimen were stressed in air below the threshold, salt water added, and then the stress increased, rapid failure occurred. If, however, the total stress were applied first and salt water then added, the properties were the same as in air. It was clear that the stability of the oxide film was very important; some alloying elements might act favourably by accelerating repassivation.

Professor Nutting spoke of the role of aluminium in titanium alloys. Some people supposed that the distribution of dislocations had no effect on susceptibility to SCC, but this was wrong. Aluminium in solid solution lowered the stacking fault energy and the dislocations became straight; this led to susceptibility to transgranular cracking. He thought that Crossley's Ti-Al phase diagram quoted by Mr Williams was thermodynamically unlikely and was incorrect. The effects found were probably due to ordered domains in the Ti-Al system, not to precipitate. It was these domains which lowered stacking fault energy and straightened dislocations. A precipitate would lead to intergranular cracking, which was not observed.

Mr Minkler said that in fact most experts in the USA would agree with Professor Nutting; and Mr Williams himself agreed that ordering could occur.

Mr W.K. Boyd supported Dr Scully's hydrides; he had propagated a crack by low stresses in an atmosphere of hydrogen. He added that Ti_3Al could not be the only cause of susceptibility to SCC because the Ti-8Mn alloy was also susceptible. To this Professor Nutting added that manganese would also be expected to order and to give the same effects as aluminium.

Mr Cotton thought that theories of the mechanism of SCC in titanium alloys had become too inflexible. Hydride formation was surely not the only mechanism. He had found SCC in highly purified CCl_4 and C_2Cl_6 which contained no hydrogen. Those who believed only in a hydride mechanism would have to accuse him of having undetected and perhaps undetectable impurities in these solvents.

Mr Williams concluded the discussion by agreeing with the statement in Mr Cotton's paper that the phenomena shown by precracked bent beam tests in salt water were "wet fracture toughness" rather than SCC as normally understood. Any modification which reduced the fracture toughness in air reduced the deleterious effect of seawater. He again emphasized the importance of processing.

STRESS CORROSION CRACKING OF VERY STRONG LOW-ALLOY
AND MARAGING STEELS: LABORATORY ASPECTS

by

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STRESS CORROSION CRACKING OF VERY STRONG LOW-ALLOY AND MARAGING STEELS: LABORATORY ASPECTS

Leno Matteoli and Tullio Songa

1. INTRODUCTION

For some decades steel manufacturers have made available low-alloy steels, of tensile strengths of more than 140 kg/mm^2 , having adequate toughness.

These steels are of great interest for the use in all cases requiring materials with high strength/weight and strength/volume ratios, as in the aerospace industry. Even more valuable are special steels with a high nickel content and with tensile strengths of 210 kg/mm^2 and more, the so-called "maraging" steels.

All these materials, and low-alloy steels in particular, have low corrosion resistance and they must, therefore, be conveniently protected. Unfortunately some treatments for surface finishing, such as pickling or electroplating, as well as cathodic protection, may cause the formation of cracks in these materials, under the action of external mechanical stresses or even, of internal stresses.

In addition, these materials show failures if they are exposed, under load, to different environments, such as chloride solutions or moist air.

In the case of failures in these materials after pickling or electroplating, or with cathodic protection, the failures can be clearly attributed to hydrogen embrittlement.

The causes of failures which take place in these materials when they are exposed, under load, to some corrosive environments, are still under discussion. In particular, it must be determined whether these failures are caused by stress corrosion cracking or if, and to what extent, they are also caused by hydrogen embrittlement.

Before examining the available data on this complex problem, a short review on the characteristics of the steels under discussion will be given.

2. MECHANICAL AND METALLOGRAPHIC PROPERTIES OF HIGH STRENGTH CONSTRUCTIONAL STEELS

Constructional high strength steels can be divided in three main groups:

- (i) Heat treatable low tempered CrNiMo steels and similar kinds: these are conventional materials such as AISI 4340 or UNI 40 NiCrMo7. For these particular applications they are subjected, however, to a tempering treatment at a

sensibly lower temperature than that indicated in conventional use. In fact, while in these last cases tempering temperature is chosen between 600° and 630°C, in use for high strength parts the tempering is carried out at temperatures even below 200-250°C, so as to obtain a tensile strength even higher than 200 kg/mm². The structure consists of low tempered martensite in which precipitated carbide is seldom resolved with an optical microscope.

- (ii) Chrome steels of the H11, H13 type, corresponding approximately to UNI UX 35CrMo5 and UX 35CrMoV5 steels: these steels have been used for a long time as hot-working tool steels (e.g., dies for die casting, for plastics, etc.) and their employment as high strength constructional steels is comparatively recent. They are tempered, after martensitic hardening, at temperatures around 520°C: by suitably choosing the tempering temperature between 510 and 650°C, tensile strengths between 140 and 210 kg/mm² can be obtained (Fig.1). Their structure consists of tempered martensite (Fig.2) with dispersed fine carbides near undissolved carbides and they owe their properties, at least in part, to phenomena of secondary hardening for precipitation of carbides during the tempering (e.g., MO_2C and V_4C_3 , Figures 3(a) - 3(b)).
- (iii) Maraging steels. These are iron alloys with a high nickel content (18, 20 and 25%) and other alloy elements, with and without cobalt, characterised by an extremely low carbon content (0.03%). Their microstructure consists of a comparatively soft martensite (diffusionless transformation of solid solution without interstitial elements) hardened with a successive treatment of precipitation hardening. Their tensile strength varies, according to type and heat treatment, between 130 and 210 kg/mm², with good ductility and toughness characteristics. These preliminary remarks show that all these materials have, as a common property, a martensitic structure, modified to a greater or lesser extent by tempering or ageing treatments. A study on stress corrosion in different environments cannot omit some preliminary remarks on the nature of these materials and on the correlations between heat treatment and mechanical characteristics: in particular, it is appropriate to draw attention to the nature of the different kinds of martensite and to the possible effects of various modifications on stress corrosion.

CrNiMo Steels²⁴

Table I gives the composition of some steels of this family. They are medium-alloy steels usually employed as heat-treatable steels. The carbon content, ranging between 0.3 and 0.4% (exceptionally 0.5%), allows us to obtain an interstitial martensite, sufficiently hard and strong after tempering: nickel and chrome ensure good hardenability (Fig.4), while molybdenum and vanadium increase the retardation of tempering and reduce the danger of tempering brittleness; vanadium, particularly, contributes to grain refining and molybdenum is an effective antidote to tempering brittleness.

For correct use of these alloys as high-strength materials, we must remember that a low-temperature tempering can bring very low values of ductility and in some cases can increase tempering brittleness. Besides, these steels, after such treatment, are very sensitive to notch brittleness, and all this obviously reduces the size of the pieces and their importance, without considering, of course, the difficulties encountered in welding.

According to Klier, however, these steels cannot be considered sensitive to brittleness: the heat treatment makes them different from the same materials treated by the conventional process and, in use, they cannot, and must not, be judged by the same criteria.

Much research has been, and still is being, done to improve the general properties of these steels without lowering their strength. The results obtained show that these improvements can be obtained by operating on different factors. Specifically:

- (a) Steelmaking processes (Aksoy¹)
 - vacuum melting,
 - remelting in consumable electrode furnaces.
- (b) Composition (Shih, Averbach and Cohen^{8,2})
 - increase in the amount of carbide forming elements,
 - increase in silicon and cobalt content.
- (c) Mechanical and heat treatments (Warke and Elsea^{9,5})
 - martempering,
 - ausforming,
 - marstraining.

In Figures 5, 6 and 7 some results are collected, showing the improvement which can be obtained by vacuum melting, in various conditions, of 4340 steel¹. It is known that these improvements are connected with the reduction of the inclusions and of residual gases: sulphur and phosphorus contents allowed by the present specifications are probably still too high as regards the weldability of very high strength steels (Randall, Monroe and Rieppel^{7,3}). In fact there is a danger of microcracking, due, most probably, to phosphorus and sulphur segregations in interdendritic areas.

Regarding the effect of composition on strength properties, two tendencies can be observed:

- (i) Increased content of carbon and of carbide forming elements (Cr, Mo, V...): this tendency has led to the development of new types, some examples of which are reported in Table I.
- (ii) Increased percentage of silicon or alloying with cobalt: these two elements on the one hand promote the retardation of tempering and on the other the lowering of Ms point (Irvine, 1962): we shall refer to this again, and will discuss methods and the mechanism of ageing the martensite.

Some of these types of steel are included in Table I: it is clear how the addition of silicon brings about a significant improvement in strength.

Altsetter, Cohen, and Averbach² have recently pointed out that silicon in CrNiMo steels is effective, not only because it stabilises carbon formation at comparatively high temperatures of the third tempering stage, but also in delaying the coalescence of cementite: silicon makes it possible, in this way, to make temperings at a higher temperature. In such conditions there is an increase in toughness without a noticeable lowering of the strength of the martensite.

In relation to control by heat and mechanical treatment, it may be said that mar-tempering makes the quenching treatment less sudden, reducing the harmful effects of strong thermic gradients.

The ausforming that can be put into effect for rolling, forging, and drawing in the metastability field of austenite (Fig. 4) (austenitic bay about 500-590°C), makes it possible to increase significantly the strength properties (Table II) without reducing the ductility and, in some cases, even improving it³³. Figure 8 shows the variation of the mechanical properties of one of these steels with tempering temperature, with traditional treatment and after ausforming³³.

With regard to marstraining (light cold deformation after traditional tempering), research by Matteoli and Andreini⁶⁰ has shown the following:

- (a) A deformation taking place on hardened CrNiMo steels, which have been tempered at a comparatively low temperature, causes an initial softening of the tempered martensite.
- (b) The initial hardness is restored by tempering at the same temperature as the first time.
- (c) The fatigue behaviour is, in practice, not influenced by the deformation of the tempered martensite.

More recently Warke and Elsea⁹⁵ have made some marstraining tests on two steels of this kind, obtaining the results of Table III.

Breyer and Polakowski¹³ have shown that by cold-forming (10%) an untempered martensite, in 4340 and 4140 steels, an increase in strength up to 280 kg/mm² with 30% reduction of area can be obtained.

Steels with 5% Chromium^{95, 77, 82}

These steels, which, at least in part, owe their strength properties to phenomena of secondary hardening, show a noticeable temperability (Figs. 9 and 10).

The secondary hardening is due to the precipitation of carbides Mo₂C and V₄C₃ during the tempering at about 520°C. They present a significant tempering resistance (Figs. 1 and 3).

As shown in Figure 1 (Ref. 36), strength values between 140 and 210 kg/mm² can be obtained, according to the tempering temperature (between 650 and 510°C), with resilience and elongation values (at equal tensile strengths) exceeding those of AISI 4340 steels. Figure 11 shows that steel with 5% chrome does not suffer a lowering of resilience at 350°C, nor an increase in ductility around 200°C, which is ascribed to residual austenite^{30, 82}.

At equal strength, fatigue behaviour seems superior to that of 4340 steels (Fig. 12). This steel has good characteristics even at high temperatures: a steel treated for a tensile strength of 185 kg/mm² at about room temperature still shows, at 480°C, a tensile strength of about 140 kg/mm². This explains its use as a high temperature tool steel.

On the other hand, as a constructional steel, it can be considered, with regard to hot applications, an intermediate between stainless steels and average strength steels, because the strength/density ratio exceeds that of most steels and even that of titanium alloys^{3, 4}.

In addition, the ausforming treatment in this type of steel can notably increase the resistance properties, as shown in Table IV (Ref.95).

Maraging Steels^{22, 83, 11, 23, 99, 72, 97}

As already mentioned, these steels, because of their composition (low carbon content and high content of nickel and other alloy elements) have a comparatively soft martensite which can be hardened by precipitation.

In Table V the composition and properties of three types of maraging, which have been set up in the Nichel Mond laboratories, are reported: martensite, obtained through tempering, has a body centred cubic lattice and the tempering (1-10 hours at 480°C) causes Ni₃Mo precipitation and an ordered phase probably composed of Fe₂CoNi.

The simultaneous presence of cobalt and molybdenum (Fig.12), as well as titanium additions, increases the mechanical resistance obtained through ageing.

An improvement of the properties can also be obtained by vacuum melting and by bringing about a plastic deformation during precipitation treatment.

Of the three types of maraging steels, the one with 18% cobalt and molybdenum presents the best combination of properties, that is

- tensile strength about 210 kg/mm²,
- high ductility and resistance,
- very low transition temperature, excellent forgeability and weldability,
- small distortion during heat treatment,
- possibility of surface hardening by nitriding with improvement of fatigue resistance.

New types of stainless maraging having outstanding stress corrosion properties have recently been introduced; in particular a very strong and ductile alloy (C ≤ 0.003%, Mn = 0.30%, Cr = 14%, Ni = 6.50%, Ti = 0.80%): these stainless chrome steels have corrosion resistance properties comparable to those of AISI 410, 430 and 304 steels and can be hardened by ageing and by cold deformation; the properties of stress corrosion resistance also seem very good⁵.

3. HARDENING MECHANISMS OF MARTENSITE

We have seen that high strength structural steels can be divided into three groups, very different in composition but all characterised by basic martensitic structure of different types (interstitial or substitutional), altered to a greater or lesser degree by tempering precipitation, or work-hardening.

More precisely:

- (a) *4340 Type Steels*: interstitial martensite obtained by normal quenching or by martempering, or after ausforming treatment: this martensite is tempered at a low temperature and can be subsequently subjected to marforming. The lattice of the martensite plates is tetragonal and the value of the axial ratio c/a depends on the carbon content and on the presence of stacking faults. In low carbon steels, martensite is formed by plates which are limited by dislocation rings, whereas in steels with higher carbon content it is formed by groups of twinned (very thin) crystals: thus the orientation relationship between primary austenite and different types of martensite can be explained.
- (b) *5% Chrome Steels*: interstitial martensite obtained by normal quenching or martempering or after ausforming treatment: this martensite is tempered at average temperature and is subjected to a secondary hardening process. It can be subjected afterwards to marforming.
- (c) *Maraging Steels*: substitutional martensite, comparatively soft, subsequently hardened by precipitation.

In every case the high resistance is given by a martensitic structure, which requires, in the first place, a complete, regular austenitising, with fine grain size; the quenching rate must be such as to avoid transformation in the bainitic and perlite fields, particularly for types (a) and (b), but not so high as to cause distortion or quenching cracks.

The toughness of interstitial martensite is substantially due to the hardening caused by the carbon atoms placed in interstitial position: as everyone knows, the increase in toughness and in resistance is particularly sensitive with carbon contents up to 0.4 - 0.6% and becomes less important for higher carbon contents.

In addition, the presence of a fine and complex structure and of lattice defects which cause internal stresses, contribute to the hardness of martensite.

The influence of the substitutional alloying elements on the toughness of interstitial martensite is not generally very important or critical (Fig. 14): Irvine⁵⁰ has proved, however, that the addition of 4% Cr, Mo, Ni, Mn increases the hardness of carbon martensites: the increase in hardness is within a range of about 100 Vickers units (Fig. 15): the decrease in hardness towards higher carbon content is due to the formation of residual austenite together with the martensite. These elements, in fact, increase the field of metastability of austenite and lower the M_s point (Table VI).

With the same composition an increase in the resistance of martensite can be obtained by grain refining, that is by reducing the dimensions of the martensite plates: this is like refining or reducing the grain sizes of primary austenite.

The most obvious and usual measure is that of avoiding, as much as possible, overheating above A_{c3} but, when the shape of the TTT curve allows, significant results can be obtained by plastic deformation of the austenite in its metastability field (ausforming): very refined martensites can thus be obtained and the tensile strength can be raised to 35-40% without sensibly lowering the toughness properties (Gullotti³³). The ausforming acts substantially by increasing the nucleation of martensite and thus

contributing to a very refined martensite, even starting from overheated austenite. Martensite refinement can sometimes be promoted by formation of microscopic pre-precipitates in the metastability field of austenite, which increases the nucleation of martensite. This is one of the advantages of marquenching, and not the least.

It is necessary, on the other hand, to remember that, when high tensile strength is required, fully martensitic steels cannot be employed: it has been seen that martensites, both interstitial and substitutional, are quite strongly modified by tempering treatments, which cause

- (a) relief of internal stress if the temperature is not very high,
- (b) carbon diffusion at average tempering temperatures,
- (c) formation of atmospheres of solute elements (secondary hardening) or pre-precipitations of elements from solid oversaturated solutions.

Generally the tempering of heat treatable steels (for example, 4340) at rather high temperatures confers the required properties of toughness, lowering the hardness and the tensile strength and increasing the ductility, whereas in tool steels (type H11) an increase in resistance by secondary hardening takes place.

The mechanical characteristics of martensite are so related to the quenching - tempering cycle that structural variations can be caused. The mechanical characteristics and the structural modifications of martensite can have a definite effect on the resistance of the material to the delayed fracture; it seems valuable therefore to analyse, even briefly, the different possibilities or ways of martensite hardening.

The hardening mechanisms of martensite can be outlined as follows⁹⁷:

- (a) Solid solution hardening {
 - with interstitial atoms
 - with substitutional atoms
- (b) Precipitation hardening {
 - Ionic compounds:
iron carbides, chrome and molybdenum carbides.
 - Intermetallic compounds:
(possibly ordered)
- (c) Short range ordering: Guinier-Preston zones (clustering)
- (d) Interaction with dislocations (atmospheres), stacking faults (Suzuki).

The first two hardening effects (by solid solution and by precipitation) can be illustrated by Figure 15, strictly relating to solution martensites (carbon interstitial and substitutional) and by Figure 16 (Ref. 97) relating to tempered martensites: this last diagram shows the additional effect of precipitation hardening; this hardening becomes considerable when the carbon content is more than 0.3%.

Tempering treatments at low temperatures in Fe-C alloys, besides relieving processes, cause the precipitation of ionic Fe_2C and Fe_3C compounds. The presence of substitutional elements affects the precipitation and it is particularly useful to know their effect. Irvine⁵⁰ has studied the effect of 1% addition of substitutional elements on the tempering retardation, by comparing the hardness variation caused by each single addition (Table VI).

Irvine observes, moreover, that an element will be the more interesting the smaller is the lowering of the M_s temperature and the greater is the tempering retardation caused by it, at equal concentrations.

Irvine has collected some information on this in Table VI. In column 4 he has calculated the rate, entirely empirical, between tempering delay and M_s lowering, considering this rate as indicative of the effects of the properties of martensite: cobalt and silicon are indicated as two of the most interesting alloy elements. The influence of silicon must be related to the fact that type Fe_3C carbide remains stable at higher temperatures during the ageing of silicon supersaturated ferrites rather than ferrites with a low silicon content⁵⁸. Silicon would show a similar effect in the course of the first tempering stage of martensite, during which metastable carbide develops.

Hardness by formation of intermetallic compounds generally takes place with rather high content of alloying elements in martensite: in carbon martensites or in medium alloy martensites the phenomenon is practically unknown and only in the last few years has it been possible to see that it takes place with a certain frequency in very high alloyed steels: it seems to be connected with a phenomenon of order-disorder transformation. These precipitates are of extremely fine dimensions (in the range of a hundredth of a micron) and can be resolved only through electron microscopy with special techniques, but they exert a considerable influence on hardening and on strength characteristics. It is assumed that sometimes it is a matter of microzones which have orderly displayed, and that it is necessary for their formation that a preliminary deformation of the lattice has taken place; this deformation is due to the presence of one or more atoms of large dimensions and to the tensile strength of the martensitic structure.

In Table VII some of the compounds present in martensites are indicated: they are steels having a particular composition and nature, but they are probably present also in the martensites of high strength steels, which are the object of our research.

4. SUSTAINED LOAD FAILURE OF HIGH-STRENGTH STEELS: HYDROGEN EMBRITTLEMENT OR STRESS CORROSION CRACKING?

We have already mentioned that high strength steels are particularly susceptible to hydrogen embrittlement.

Hydrogen embrittlement differs from other forms of embrittlement because it does not affect the results of high rate mechanical tests, e.g. impact tests, and it affects in a comparatively moderate way also the results from tensile or bend tests. In addition, hydrogen embrittlement seems to be moderate or absent at low or very high temperatures and a maximum at intermediate ones.

The typical failure produced by hydrogen embrittlement is the occurrence of delayed fractures under sustained load, with load levels considerably lower even than the proof stress levels. This type of failure is sometimes called "static fatigue"; leaving the name "fatigue" to dynamic failures, a better name for it is "sustained load fracture" or "stress cracking".

The characteristics of hydrogen cracking⁸⁶ are

- (a) a specific incubation time before crack initiation,
- (b) a minimum stress below which delayed failure does not take place,
- (c) discontinuous crack propagation,
- (d) an acceleration of the embrittlement by cathodic polarisation,
- (e) a reversibility of the incubation time, with respect to applied stress.

Of these characteristics, (d) and (e) are peculiar to hydrogen cracking.

The higher is the tensile strength of the steel, the more pronounced is its sensitivity to hydrogen embrittlement. For this reason, hydrogen cracking is a typical phenomenon for the materials concerned.

The presence of hydrogen in steel also increases its notch susceptibility, which is generally higher, the higher is the tensile strength of the material.

As all structures show stress concentration at some points, this aspect of the problem is, of course, of great practical importance and demands thorough evaluation in choosing materials and their treatments.

Hydrogen susceptibility of high strength steels requires particular caution in surface finishing; the use of mechanical cleaning methods is to be preferred to acid pickling and in electroplating an accurate selection of bath composition as well as of operating and after-treatment conditions is needed, in order to minimize hydrogen adsorption.

An interesting collection of data on this subject can be found in the proceedings of the symposium held in 1966 by the American Electroplater's Society⁷⁴.

Of course, with materials susceptible to hydrogen embrittlement the use of cathodic protection with impressed currents as well as with sacrificial magnesium anodes is not advisable.

Hydrogen adsorption can generally take place whenever a metal is subjected to hydrogen corrosion. The hydrogen adsorption is, however, particularly relevant when "poisons", such as some sulphur and arsenic compounds, are present. These substances, possibly produced, during the attack, by the reaction of non-metallic inclusions, might act as inhibitors of the association of hydrogen atoms, making the adsorption easier.

In the case of high strength ferrous materials, mainly low and middle alloy steels, the exposure to acid environment containing compounds of the type previously indicated causes, under the action of service stresses, mainly transcrystalline cracks as, for instance, in parts operating in contact with acidic water containing hydrogen sulphide (Refs. 75, 93, 12, 28, 94, 6 and 29).

These failures now attributed⁹¹ to hydrogen cracking, i.e. to mechanical phenomena, were at first supposed to be due, at least in most cases^{93, 12}, to stress corrosion processes, which were made easier by the presence in the structure of a network, presumably of non-tempered martensite. By these mechanisms the fracture would therefore have taken place through more direct action of the corrosive attack. Discussion is needed on this question.

It has been observed that hydrogen, which is discharged on some metallic materials, can be absorbed in the lattice and can make the material sensitive to fracture when the metal is subjected to mechanical stresses (internal or external). If the hydrogen evolution takes place by the working of a corrosion cell and if the mechanical stress is acting simultaneously to the corrosion process (so that the fracture also occurs during this process) the whole phenomenon assumes all the outward characteristics of a stress corrosion phenomenon.

The outward similarity of both phenomena has prevented, and still does prevent, us from clearly establishing, in many cases, to which of these two causes the fracture under load of a metallic material in a corrosive environment is to be attributed.

As an example, it will be remembered that one of the oldest theories brought forward as an explanation of the stress corrosion cracking phenomenon which had first aroused the attention of technicians and scientists, the so-called "caustic embrittlement", consisted in thinking that the fractures were due to embrittlement by hydrogen produced by the reaction between iron and alkaline solution at high temperature.

In order to distinguish between these two types of phenomena, which Harwood³⁹ would like to combine into single concept, through a wider interpretation of the meaning of stress corrosion cracking ("a cracking resulting from the combined effect of corrosion and stress" - Reference 89), it is necessary to discuss the nature of the two phenomena. The next section gives a brief survey of the mechanisms proposed to explain hydrogen embrittlement cracking; for the mechanisms proposed to explain the stress corrosion cracking, reference is made to the general report (Fontana). It will suffice here to remember that the interpretation of the cracking process as being due to a rapid corrosive attack on the specimen made anodic by the mechanical stress is not now generally acceptable.

In fact, the change of potential induced in a metal by cold-working⁹⁰ or by elastic strain⁹³, is very moderate.

Besides, the current densities at the end of the crack necessary to produce the usual rapid crack propagation would be too high. In general, it can be said that a mechanical stress and a chemical, or electrochemical, action occur in the phenomenon more or less alternately, a theory whose basis was expressed by Dix²⁶ in 1940.

On the whole, it can be said that, according to the modern view, chemical and electrochemical actions give rise to fractures by creating initial points of attack, possibly along preferential pre-existent paths, which act as stress raisers. Mechanical stresses cause the crack to continue and also cause the breakdown of protective coatings, or the formation of local segregations, which subject the material to localised attack.

According to a recent theory, the specific action of the electrolyte could also consist in a localised adsorption of some chemical species which foster the spread of fractures by a mechanism which will be explained in detail later. This mechanism, which was first proposed⁶⁶ to explain hydrogen embrittlement failures, has been termed⁹⁰ "interfacial stress cracking" or "stress sorption cracking".

5. MECHANISMS OF HYDROGEN EMBRITTLEMENT IN STEEL

The first theory proposed in order to explain hydrogen embrittlement was the so-called "planar-pressure" theory advanced by Zapffe¹⁰³. According to Zapffe^{100,101}, atomic hydrogen enters the metal remaining dissolved in the lattice, as an atom or an ion H^+ , the amount being dependent on the temperature and the pressure according to Henry's law. A balance between atomic hydrogen in the lattice structure and gaseous hydrogen cut of it, is built up; owing to this balance, the pressures of gaseous hydrogen are very high*.

Molecular hydrogen can precipitate into defects of the lattice structure or in "planar" separations and therein build up pressures sufficient to cause lattice distortions, with blockage of slip planes and subsequent embrittlement.

Upon straining, the voids enlarge and the hydrogen pressure drops; therefore, in order to maintain the embrittled condition, a further diffusion of hydrogen into the voids or defects is necessary. If the plastic deformation takes place very rapidly, there is insufficient time for a further hydrogen diffusion and the embrittlement decreases.

The effect of temperature could be explained since the pressure of a gas phase also decreases with decreasing temperature. Thus there will be a critical temperature, and a critical rate of cooling, for any given set of conditions, such that the critical embrittlement pressure pH_2 is decreased more rapidly than it is replenished by precipitating H and embrittlement is seen to decrease.

Petch^{66,64,65} is interested in crack mechanism and applies Griffith's theory on brittle fracture to the case of hydrogen. According to Petch, the crack propagation arises from micro-cracks ahead of an array of dislocations piled up against a grain boundary. Hydrogen absorption on the crack surface causes a decrease in surface energy and reduces, according to Griffith's theory³², the stress required for the fracture to take place.

The quantity of hydrogen absorbed in this way is controlled by the diffusion, which might explain why hydrogen embrittlement depends on the rate of plastic straining and on temperature.

This phenomenon has been called, as we have already seen⁹⁰, "interfacial stress cracking" or "stress sorption cracking".

* The relation between hydrogen dissolved in the lattice (x , ml/g), temperature (T , °K), and equilibrium pressure of gaseous H_2 (p , atm) has been given by Phragmen⁶²:

$$T = \frac{3000 - 0.062p}{\log p - 2 \log x + 3.60}$$

The pressure of gaseous hydrogen at the thermodynamic equilibrium with a given amount of dissolved hydrogen increases with decreasing temperature. For instance, the hydrogen pressure for 5 ml H_2 /100 g dissolved in the lattice at 600°C is 17 atm; at 300°C, 580 atm; at 200°C, 4080 atm; at 100°C, 10,870 atm; at 23°C, 17,500 atm.

According to Bastien^{6, 7} hydrogen, which enters the metal as proton, collects round dislocations in the form of a Cottrell's atmosphere and accompanies the dislocations in their movements during plastic deformation, causing local oversaturation of hydrogen, with a build-up of pressure in the voids, caused or enlarged by the deformations and by the strain round them.

For the proton to follow the dislocations in their movement, the diffusion rate of the proton must be greater than, or equal to, the movement rate of the dislocations; that would again explain the effect of temperature and the rate of the plastic deformation on the occurrence of hydrogen embrittlement.

As a result of roentgenographic researches^{70, 71}, Bastien's assumption is that hydrogen localises preferably in (112) planes and exactly at the centre of a tetrahedron made up of iron atoms, a position that corresponds to the one assumed for carbon in α iron (Fig. 16).

Such a localisation, according to Bastien, might further explain the absence of embrittlement in those metals and alloys whose (112) planes are not slip planes, and its disappearance in α iron at a low temperature, in which conditions the planes (112) are no longer active slip planes.

De Kazinczy's theory²⁵ starts from the assumption that, because of energy fluctuations, there is always in a metal a tendency for a crack to appear at the tip of dislocation arrays, although at low stresses the crack will disappear again. If hydrogen can diffuse into an unstable crack, the energy conditions will change and the crack will be stabilised at a stress level that depends on the hydrogen pressure, i.e., the hydrogen activity of the lattice. The same reasoning can be applied to shear fracture.

In a metal containing hydrogen, part of the total energy of a test piece consists of the energy content of the gas in the cracks. On crack propagation the gas will expand with a corresponding release of energy. The released gas energy is added to the released strain energy; hydrogen will thus lower the external stress at fracture.

With a very high rate of crack propagation, the gas can only expand adiabatically, and the lowering of fracture stress, under these conditions, can only be slight. To obtain a greater lowering of the fracture stress, fresh hydrogen has to diffuse into the crack simultaneously with crack propagation if the spreading of the crack is to continue. The lowering of the external fracture stress will be determined by the initial gas pressure, but a certain amount of gas has to diffuse into the crack. The process of fracturing can thus be divided into two successive periods. During the first, the crack spreads slowly, the rate being determined by the rate of hydrogen diffusion; when the crack has grown sufficiently by this process, a second period can begin, the crack then propagates with adiabatic gas expansion at a very high rate.

When the external stress increases, instead of remaining constant, during the first period, the second period will begin and fracture will occur at a higher external stress than that at which crack propagation started. This explains why hydrogen embrittlement is less under impact tests or under tensile tests at low temperatures. The testing temperature has yet another effect. If there is plastic deformation at the surface of the crack this will be a decreasing function of the rate of crack

propagation. When the temperature is lowered the hydrogen diffusivity decreases, resulting in a decreased rate of crack propagation during the first period. The total amount of work which must be done by external stresses and gas expansion will thus increase. Less hydrogen embrittlement will be observed at low temperatures, even at very low deformation rates.

As pointed out by Troiano⁴¹, the theories advanced to explain hydrogen embrittlement have similar features, although the mechanisms proposed are different. All the authors, in fact, postulate a lattice involving defects, which are termed voids, or lattice rifts or Griffith's cracks, or piled-up dislocations, producing cracks.

The implicit assumption is made that the voids are very large when compared with the volume of the lattice unit cell and that, within these voids or on their surface, hydrogen localises. Such a localisation appears necessary since embrittlement is shown at very low hydrogen contents.

The specific details of the embrittlement mechanism depend on whether the hydrogen at the void surface or in the void is assumed to be embrittling.

Zapffe, Bastien and Azou, and De Kozlaczky assume that hydrogen in voids is damaging, whereas Perch and Stables believe that embrittlement is caused by hydrogen absorbed in the void or crack surface.

Troiano's theory is concerned with hydrogen diffusion in the lattice and its behaviour in the areas subjected to plastic deformation. If a metallic material is deformed, hydrogen diffuses to the highly stressed region and concentrates there; a steep hydrogen-concentration gradient may be created by a severe stress state.

Mechanical tests are usually performed at relatively slow strain rates; thus, ample opportunity exists for the creation of a severe concentration gradient in the triaxially stressed volume. As the stress continually increases, the critical combination of hydrogen concentration and stress state may be attained, and a crack opens in the lattice at the point of maximum triaxiality.

The magnitude of the concentration gradient created in the triaxially stressed region depends primarily upon three factors: (a) the initial hydrogen concentration, (b) the hydrogen diffusion rate, and (c) the time during which hydrogen may diffuse.

The disappearance of hydrogen embrittlement at low temperatures results from decrease in the hydrogen diffusion rate with decreasing temperature. Although the stress-induced driving force is presumably independent of the temperature, the mobility of the atoms at low temperatures is strongly retarded; thus the embrittlement decreases.

The disappearance of hydrogen embrittlement at high temperatures can be explained on the basis of the competing effects of the stress-induced driving force, which tends to promote concentration of hydrogen in the triaxiality region, and the classical concentration-equalising force which promotes homogenisation. At high temperatures, the homogenising force, which increases with temperature, is sufficient to overpower the stress-produced gradient, which is temperature-independent, with the result that the embrittlement decreases. It should also be noted that the notch sensitivity of the steel decreases with increasing temperature, thus, the voids should be less effective in creating a region of severe stress state.

The strain-rate dependence of hydrogen embrittlement reflects variations in the time available for hydrogen to diffuse into the highly stressed regions. In a fast strain-rate test there is insufficient time for a damaging quantity of hydrogen to diffuse into the region of maximum triaxiality and embrittlement is minimised. However, with decreasing strain rate, more hydrogen can diffuse into the highly stressed region and embrittlement increases. The proposed mechanism is thus compatible with the known effects of temperature and strain rate.

Troiano's theory on the preferential diffusion of hydrogen to the most highly stressed zones can explain the effect of hydrogen on notch sensitivity. Hydrogen migrates to the regions near the notches where there is a maximum of triaxial stress and where the probability of forming micro-cracks is also at a maximum. The pressure of molecular hydrogen in these cracks at equilibrium conditions will be much higher than the one which might be reached if hydrogen were uniformly distributed in the whole lattice. Near the cracks, the triaxiality will thus be maximum and the crack can propagate without appreciable plastic deformation of the surrounding material. The energy required for crack propagation will be lowered, both for lack of the amount required for plastic deformation and for Petch and Stables's sorption phenomena. According to De Kazinczy, part of the energy required for crack propagation will be supplied from the hydrogen gas which, as already said, will be present in the crack at high pressure. Naturally, this effect will always take place in real materials, which always contain voids of various kinds. The effect will be more or less pronounced as a function of the geometry of the defect.

6. METHODS OF DISTINGUISHING HYDROGEN EMBRITTLEMENT FROM STRESS CORROSION CRACKING

It has been seen that in a material subjected to the simultaneous action of corrosive attack and mechanical stress, possible fractures, which present similar features, can be due either to stress corrosion or to hydrogen embrittlement.

The problem of the distinction between stress corrosion failures and hydrogen embrittlement failures is very important, in order to choose the most appropriate means of protection. While, in fact, in the case of stress corrosion cracking it is possible to slow down or to stop the crack propagation by means of cathodic protection, in the case of hydrogen embrittlement failures the application of a cathodic current may emphasize the phenomenon, as we have already said.

The only way to differentiate clearly between these two cracking mechanisms seems to be the method of polarisation, which offers the advantage of reproducing under controlled conditions, and in a short time, what happens during long periods of exposure, at service conditions.

This method is based on the concept that, if the fracture is caused by a corrosion which proceeds along an active path, the application of a cathodic current, which reduces the entity of the corrosion, increases the time-to-fracture. Still, in this case, the application of an anodic current brings about an opposite result even if, when an anodic current is applied, it is not possible to predict exactly the effect of the current on the time-to-fracture, because the anodic current can produce a more general attack, by increasing the anodic area⁶⁸.

Conversely, if the fracture is caused by the adsorption of hydrogen, possibly generated at the cathode of a corrosion cell, the application of a cathodic current, with subsequent hydrogen generation, shortens the time-to-fracture, whereas the application of an anodic current brings about a limitation in the development of hydrogen with subsequent increase in the time-to-fracture.

One of the first applications of this technique was made on a type AISI 410 stainless steel¹⁵ which, subjected to a small cathodic current, showed an increase in time-to-fracture. By such an observation it has been possible to infer that this type of steel breaks, without impressed current, according to a stress corrosion mechanism.

A typical example of this technique is the test made by Phelps and Loginow⁶⁷ on a 12 MOV stainless steel, tempered at 420°C under strain in an aërated 3% NaCl solution at room temperature. The influence of anodic and cathodic polarisation on the time-to-fracture is shown in Figure 18. We see that the anodic polarisation reduces the time-to-fracture from 200 minutes, when no current is applied, to 20 minutes, when the current density is 0.93 mA/cm².

On the contrary, with low cathodic current densities, the time-to-fracture increases significantly (about 27,000 minutes at 0.02 mA/cm²).

With current densities higher than 0.02 mA/cm², the time-to-fracture lowers again, to become about 10 minutes at a current density of 0.93 mA/cm². Such behaviour indicates that, without current polarisation, with anodic polarisation, and with cathodic polarisation at low current densities, the fracture observed is caused by stress corrosion, whereas, at current densities higher than 0.02 mA/cm², hydrogen adsorption takes place and fracture is due to mechanical causes.

The polarisation method which appears correct, at least in principle, has been applied by many authors.

Conflicting results, obtained by some authors⁸⁸, could be attributed⁸⁸ to an incorrect interpretation of the test results.

Many authors have tried to establish whether a diagnosis about the mechanism of a fracture could be made through a metallographic examination. The results, as shown later, have not been conclusive. It seems that interesting results may possibly be obtained through an appropriate use of the techniques of electron microscopy, but much work has still to be done before a thorough evaluation of this possibility can be made.

7. STRESS CORROSION OF HIGH STRENGTH LOW-ALLOY STEELS

As we have already seen, low-alloy steels with a high mechanical strength are susceptible to delayed fractures, not only when they are previously subjected to a hydrogen charging (see, for example, Reference 86), but also when they are exposed under load to particular corrosive environments.

7.1 Corrosive Environments

The typical environments which cause fractures in these types of steels under load are those rich in chloride, such as hydrochloric acid solutions^{47, 48}, sodium chloride solutions^{67, 19, 20, 45, 79, 47, 48, 49, 59, 85} or marine atmosphere⁶⁷.

Time-to-fracture, at equal conditions, is smaller in acid solutions than in neutral solutions, as observed on a 5% chrome steel⁷⁹, on an En 26 steel^{79, 37, 48} or, at the boiling point, on a 4340 steel⁸⁵.

Fractures of this kind, however, appear also in less aggressive environments and have been observed^{8, 38, 51, 62}, on pre-cracked test specimens, in distilled water, in moist air in hydrogen gas³⁷ and even in argon, although time-to-fracture in argon decreased with increase of the dew point of the gas mixture.

7.2 Relationships Between Crack Formation and Crack Type, Structure and Heat Treatment

Several authors have tried to establish whether the crack path is intergranular or transgranular. The problem, from a metallographic point of view, is rather complex.

It has been observed that cracks are generally intergranular following the prior austenite grain boundaries but that sometimes they follow a mixed path (Figs. 19-21, Refs. 67, 19, 20, 47, 48). It has also been observed that primary cracks often initiate from non-metallic inclusions (Fig. 22, Refs. 19 and 20) and can also be followed by purely mechanical fractures⁴⁹.

In the case of attack in an acid medium the inclusions might favour the adsorption of hydrogen in the metal due to local formation of "poisons" such as H_2S . The influence of sulphur and phosphorus on the delayed fracture in acid solution has been proved in laboratory tests made in an acid medium on low-alloy steels having either different sulphur and phosphorus content or small amounts of FeS on their surface^{41, 42}.

Other researches^{47, 46} have proved that the localisation of the fractures should be connected to the presence, in the structure of fine precipitates, presumably carbides ϵ (Ref. 78). These carbides deposit preferably at the grain boundaries of austenite even if the continuity of the deposit would not seem essential to the crack propagation (Figs. 23 and 24, Ref. 62).

During the tests on a 4340 steel under load in an acidified solution of 3% NaCl (Ref. 85) it has been observed that the fractures initiated at pits, which preferably formed in zones lying near ϵ carbide (Fig. 25).

The preferential attack might also be due, in this case, in analogy with the theories being advanced to explain intergranular stress corrosion of carbon steel^{90, 98}, to local changes in composition caused by micro-stresses being generated by the presence of precipitates.

Besides, as carbides easily adsorb hydrogen (Berg, 1961) their presence might cause local variation in the concentration of hydrogen, which might promote the fracture. The fact that an increase in silicon in these carbides seems to diminish their faculty of adsorbing hydrogen might explain⁸⁵ why 300 M steels are, at equal conditions, less sensitive to hydrogen embrittlement than 4340 steels, which have less silicon content.

Lastly, fractures intergranular as to prior austenite grains have been detected²⁰ also on test specimens which had been broken by impact, in a not particularly corrosive environment. This fact suggests a possible purely mechanical action which the carbides might exert on crack propagation.

The time-to-fracture on test specimens exposed under load to corrosive environment varies, under equal conditions, with the variation of the temperature at which the material has been tempered. For example, systematic tests on Airsteel X 200 (Ref. 67) have shown that this material has a maximum sensitiveness in 3% NaCl solutions, if tempered at 150°C, and a maximum sensitiveness in sea atmosphere, if tempered at 315°C (Fig. 26), whereas, with increasing tempering temperature, the time-to-fracture increases. The increase in resistance to fracture under sustained load in an aggressive environment with increasing tempering temperature is a phenomenon which can be considered general in a neutral environment, whereas in an acid environment, as observed on En 26 in HCl 0.1N (Refs. 47 and 48), inversions have been noted.

Since, by increasing the tempering temperature to 250-300°C, ϵ carbides change into ferrite and cementite, the fact that generally the susceptibility to delayed fractures decreases with increasing tempering temperature, might appear as further proof of the existence of a relationship between the presence of carbides ϵ and the susceptibility to delayed fracture.

7.5 Influence of Mechanical Stress Level on the Appearance of Fractures

Besides the mechanical properties of steel, the stress level to which the steel is subjected is important in the appearance of cracks.

According to some authors there is a stress threshold below which no fracture would occur, as shown, for example, in References 47 and 48 for En 26 in chloric acid 0.1N and in 3% NaCl.

Lastly, it must be noted that the resistance to delayed fractures is increased if the specimens are subjected to shot-peening^{19, 45}. This result does not seem to be due exclusively to the presence, on the surfaces of the media, of residual compression strains left by the treatment, but to the fact that the treatment causes a sealing-up of the surface micro-fractures of the metal¹⁹.

7.4 Cause of Fractures

Authors do not yet completely agree whether the appearance of fractures under sustained load in these steels is due to stress corrosion cracking phenomena or to hydrogen embrittlement.

Some authors⁴⁷ observed that, in the case of En 26 steel in HCl 0.1N, a reversion in the curve time-to-fracture as a function of tempering temperature took place, as already pointed out; this phenomenon did not occur with the same steel in neutral sodium chloride solution, but had been verified⁵⁶ on specimens previously subjected to cathodic treatment.

For this reason, the authors mentioned had come to the conclusion that, in the case of neutral solutions, delayed fractures were to be considered as caused by stress corrosion, whereas in the case of acid solutions, they were to be considered as caused, at least mainly, by hydrogen embrittlement. These conclusions have been confirmed by the same authors⁴⁸ by using the method of polarisation (Fig. 27). By the same method it has also been found that delayed fractures of 5% chrome tool steel in 3% NaCl solution at pH 6 was due to stress corrosion.

It must also be pointed out that, in tests made on 5% chrome steels, exposed to a sea atmosphere and protected by different types of coatings (electrolytic coatings, paints with metallic pigments, metallic coatings obtained by displacement, etc.), the deposits have appeared efficient, whereas in sodium chloride solution they were anodic as to the steel, which led to the assumption that, in the sea atmosphere, fractures were due to stress corrosion rather than to hydrogen embrittlement⁶⁷.

On the other hand Hanna, Troiano, and Steigerwald³⁸, having observed in tests on 300 M steel in distilled water that the application of cathodic polarisation to the specimens, the addition of arsenic compounds to the water, and the de-aeration of water (Fig. 28) lowered the time-to-fracture, have now come to the conclusion that, in this case, the fractures were due to hydrogen embrittlement. This conclusion was confirmed, according to the authors, by the fact that the incubation times before the appearance of the fractures were reversible, that is, it had been observed that specimens which, during the test, had already gone through the incubation time, when taken out of the test and subjected to a sufficient period of ageing, had to go through a new period of incubation before cracking, if re-tested.

Moreover, for morphological reasons, that is, for the fact that fracture on 4340 steel tested in boiling 3.5% NaCl solution seemed to initiate from the inside of the metal, rather than from the surface, it has been thought that, in these conditions also, the fracture was due to hydrogen embrittlement. In the explanation of the mechanism of failure, the occurrence of stress-sorption cracking phenomena could be of great importance. This mechanism seems particularly to fit in the explanation of delayed fractures in hydrogen gas as well as in other media.

Some authors have tried to establish whether there are notable differences, from the metallographic point of view, between hydrogen embrittlement fractures, obtained on cathodically polarised specimens, and fractures in neutral solutions, these last being considered as due to stress corrosion. Generally, no substantial differences have been observed^{19, 47, 48, 49}, thus it has been thought that at least the active paths of stress corrosion coincide with the weaker paths of the mechanical fractures due to hydrogen embrittlement or to stress sorption phenomena and that, therefore, in crack propagation both phenomena have similar characteristics.

8. STRESS CORROSION CRACKING OF MARAGING STEELS

8.1 General

Maraging steels present in sea water a corrosion rate which is about the same as that of low-alloy steels. This happens because in both cases protective coatings do not form in sea water; so that the mechanism which controls the process is the cathodic reaction, i.e., the reduction of oxygen.

In different atmospheres maraging steels present a general corrosion resistance which is better than that of high-strength low-alloy steels. In spite of this, it is often required that the structures, which have to be put into service, are protected. The need for protection sets the problem of hydrogen cracking. Tests under load in 3% NaCl made on specimens subjected, for different periods, to cathodic treatment have shown, for example, the susceptibility to fracture of the specimens which had been subjected to the stronger cathodic treatment (Table VIII, Ref. 54).

It seems, however, that maraging steels are more resistant than other materials to hydrogen embrittlement and that they undergo faster processes of dehydrogenation in furnaces^{41, 42}. Besides, as already mentioned, maraging steels, when subjected to sustained load in particular environments, also show delayed fractures, as well as high-strength low-alloy steels.

8.2 Corrosive Environments

The results show that the resistance to delayed fracture of maraging steels exposed to industrial and marine atmosphere is quite good (Table IX, Ref. 21) and varies with the severity of the corrosive environment⁸¹. In sea water, both natural and artificial, maraging steels have generally offered a good resistance to delayed fracture (Table X, Ref. 21) and in any case better than that offered by high-strength low-alloy steels^{81, 45}.

However, in some tests made in 3% NaCl solution, some low-alloy steels, such as Rex 539 and En 30 B have offered a better resistance than a maraging 18% nickel steel of the "110 ton" grade (Table XI, Ref. 87).

It has been observed³⁰ that the susceptibility of 18% nickel maraging steel in a solution of sodium chloride varies by varying the concentration and the pH of the solution.

In particular, the time-to-failure curves, correlated to the pH, show a minimum in the pH range between 11 and 12 (Fig. 29). The figure clearly shows the effects of NaCl content on the position, the intensity, and the shape of the minimum. With increasing NaCl content, the minimum both widens and deepens and moves to lower times-to-fracture and to higher pH values. The pH value which corresponds to the minimum time-to-fracture has been proved to correspond to the onset of passivation of the metal and is due to the fact that, in this pH range, the corrosion currents generated at the remaining active areas become progressively more intense and lead to nucleation of a site susceptible to stress corrosion cracking. Change of the minimum with increasing concentration shows the depolarising effect of the Cl⁻ ion.

Tests made under sustained load in distilled water⁸¹ have shown that, even in this environment, 18 and 20% nickel maraging steels behave better than high-strength low-alloy steels.

While studying the resistance to delayed fracture of an 18% nickel maraging steel and of two low-alloy steels in distilled water at different temperatures, it has been observed that, with increase of temperature, the time-to-fracture decreases. This effect is much more evident in maraging steels than in low-alloy steels (Fig. 30, Ref. 81).

Bent-beam specimens have been exposed to 0.25% sodium dichromate and 4% soluble oil solution. One sample of 18% nickel maraging steel with 0.62% Ti showed marked susceptibility to delayed fracture in both environments, while an 18% Ni sample with 0.50% Ti failed only in the soluble oil solution.

Tests made in a trichloroethylene environment⁸¹ have shown that this medium is very aggressive; the fractures are wide and straight, with blunt tips, as if a chemical dissolution had occurred.

Lastly, other tests have been made in a 6% NaCl and 1.5% Na₂Cr₂O₇, boiling solution and in a 5% acetic acid solution saturated with H₂S at room temperature⁸⁹.

It has been agreed, in these tests, that in the chloride and in the sodium dichromate solutions the failures were due to stress corrosion cracking and that in the acetic acid solution saturated with H_2S the failures were due to hydrogen embrittlement. It has been observed that, in a chloride plus sodium dichromate environment, the fractures did not occur or were more delayed than in the acetic acid environment (Tables XII and XIII).

8.3 Appearance of the Cracks

It has been observed that the fractures shown by maraging steels failed by stress corrosion cracking in sea water or in industrial atmosphere usually have paths intergranular as to prior austenite²¹. Figure 31 shows, for example²¹, intergranular microfractures in specimens which had not shown fractures during the test period and which extended towards the core of the sample. Intergranular cracks have also been observed on steels cracked under sustained load in a distilled water environment^{45, 81} as well as in 3% NaCl solution and in tap water⁸¹.

Transgranular fractures have, however, been noted on specimens of an 18% nickel maraging steel, exposed to industrial atmosphere or immersed in a 3% NaCl solution, when strained to a stress level equal to 90% of 0.1% proof stress⁸⁷. According to these authors, the fractures occurring in less critical environments, for example, in atmosphere, often show blunt crack sides, which suggests the presence of a slow attack also on the sides of the cracks. In the case of more rapid fractures or transgranular fractures, the cracks are narrow and sharp.

A microstructural examination of stress corrosion cracks and hydrogen cracks shows that stress corrosion cracks resembled hairlines, whereas there are rounded voids along cracks caused by hydrogen (Figs. 32, 33, 34, 35).

8.4 Effect of Composition

The existing data on the effect of the chemical composition of maraging steels on the resistance to delayed fracture are very few.

In some cases²¹ it has been observed that 25% Ni maraging steels showed a better resistance to delayed fracture than 20% Ni steels.

Stress corrosion tests on two 18% Ni steels, annealed and aged, having respectively 0.029 and 0.004% C, have not indicated any effect which might be attributed to the different carbon content⁸⁰.

An increase in titanium content from 0.23 to 1.00% seemed, on the other hand, to increase the susceptibility of the steel to delayed fracture⁷⁹; this susceptibility might even be increased by the absence of such elements as boron and zirconium²¹. This is presumably because, in maraging steels having no additions of these elements, a precipitation of a grain boundary phase was thought to occur, promoting intergranular corrosion.

To explain the differences in behaviour often observed between several heats which were not substantially different, it has been thought, by analogy with what has been observed on high-strength low-alloy steels⁴¹ that the presence of some trace elements can be important in determining the susceptibility to fracture, as these impurities act as cathodic poisons and promote hydrogen adsorption⁸⁷.

Thus it seems very important that sulphur and phosphorus are contained in maraging steels in very small amounts⁴¹.

On the whole the data available do not establish a clear relationship between the chemical composition of maraging steels and their resistance to delayed fracture.

8.5 Structure and Heat Treatment

The resistance of maraging steels to delayed fracture is strongly influenced by their thermal history.

Some tests⁸⁰ have shown that the susceptibility to fracture of some specimens of 18% Ni maraging steels, subjected to a stress of about 60-65% of the yield strength, was greater both in chloride and sodium dichromate solution and in acetic acid and H₂S solution, when the annealing treatment at 1500°F (816°C) was followed by a three hours ageing treatment at 900°F (483°C), which more than doubled the yield strength of the steel, in comparison with the same steel when only annealed (Tables XII and XIII).

Further data on the effect of heat treatment on delayed fracture have been obtained²¹ on U-bend specimens of an 18% Ni maraging steel, with yield strength around 250 lb/in², immersed in an aerated 3.5% sodium chloride solution, pH 6.0, at room temperature. It has been observed that specimens annealed at 1500°F (816°C) and maraged showed no sign of cracking after 30 days on test. Specimens given 2200°F (1204°C) solution annealing treatment, and then maraged, cracked rapidly (Table XI).

This heat treatment produced significant grain growth, so that results tend to confirm previous indications that coarse grain size is harmful.

Specimens cooled to and held at 1400°F (760°C) from the 2200°F (1204°C) solution annealed, and then maraged, were even more susceptible to stress corrosion cracking. This laboratory heat treatment would maximise precipitation at grain boundaries, which is extremely harmful to both mechanical properties and resistance to stress corrosion cracking. Lastly, it appears that cold-rolling before maraging breaks up the coarse grain structure and is beneficial.

The results of a test programme, to examine the influence of tempering temperature on delayed fracture, show that an increase in tempering temperature between 400 and 485°C improves the resistance to delayed fracture (Fig. 36, Ref. 14).

In another series of test made on a 12% MgCl₂ solution, boiling at 154°C, the specimens of an 18% Ni maraging hot-rolled steel, brought up to and held for two hours at 850°C, quenched in oil and then tempered for three hours at three different temperatures (425, 480, and 525°C), show⁵⁷ that the time-to-fracture increases with lowering of stress and is much greater for the specimens tempered at the highest temperatures, with a rate of about 1 to 20, at equal stress, when the comparison is made between 425 and 525°C.

The three temperatures have been chosen to obtain an increasing amount of stable austenite. Thus it seems proved that stable austenite plays a favourable role. These results must not, however, be applied to higher tempering temperature: the results of tests made in NaCl have shown, in fact⁵⁷, that tempering at a temperature over 550°C implies a more rapid attack than tempering at 440-480°C.

The key to good resistance to stress corrosion cracking is fine grain size, grain boundaries free of harmful precipitates, and absence of composition gradients in the vicinity of prior austenite grain boundaries²¹.

There are no reliable data on the nature of precipitate compounds at grain boundaries. These phases might be intermetallic compounds between iron and the different alloy components.

The precipitation of the intermetallic compounds, responsible for the hardening, may possibly play an important role, since an overaged condition favours resistance to stress corrosion cracking⁵⁷.

In spite of this, it has been noted⁸⁰ that, at equal rate between applied stress and yield-strength-limit, steels having a better strength, particularly in an annealed and overaged condition, are more susceptible. This treatment cycle, in fact, rises strongly the yield-strength-limit.

Lowering the applied load increases the time-to-fracture; however, data confirming the existence, in maraging steels, of a minimum limit load below which no delayed fracture occurs, have not been found.

8.6 Nature of Delayed Fracture in Maraging Steels

Tests made on maraging steel specimens cathodically protected in sea water²¹ at different potential levels have proved that a slight cathodic polarization can sometimes increase the time-to-fracture, whereas by increasing the absolute potential level a faster cracking is obtained. In another case⁸¹ the use of zinc base coatings has caused maraging steels to fail more rapidly in aerated salt water and in high humidity environments than without coating. Failures of alloys cathodically protected in sea water were therefore probably caused by hydrogen embrittlement rather than by stress corrosion cracking, whereas without polarization, failures occurring in sea water were probably to be attributed to stress corrosion cracking.

At this point it has to be observed that, whereas in tests made on high-strength low-alloy steels many Authors have studied the causes of fracture either by observing the behaviour of the specimens subjected to cathodic or anodic polarization or by making other observations in the tests made on maraging steels the Authors have generally preferred to study the fracture by assuming nearly as a matter of fact that in some environments (ex: acid sulphide solutions) the fractures are caused by hydrogen embrittlement and in others (ex: sea water, atmosphere) by stress corrosion cracking.

9. CONCLUSIONS

Owing to the great range of compositions in ultra-high-strength steels and the differences in metallographic structure which these steels can obtain through heat treatment or plastic working, the number of varieties in this field has practically no limit. If to this extreme variety of initial materials we add the variety of testing conditions (size of the specimen, strain rate, nature of the environment, temperature, etc.), the prospect is even more complex.

On the other hand, the materials of interest have been either recently used as structural materials (low-alloy steels) or only recently studied and introduced (maraging steels).

It is therefore easy to understand why, although some work on this subject has been published, particularly in the last few years, our knowledge in this field is still very far from complete.

However, on the basis of all the facts gathered, the following data might be considered as acquired:

1. Low-alloy steels, as well as maraging steels are subject to delayed fracture.
2. Generally, maraging steels have a higher resistance to delayed fracture than low-alloy steels.
3. The occurrence of delayed fractures is much more frequent the greater is the tensile strength of the steel and the stress to which the steel is subjected.
4. Although there are cases of mixed paths, the path of delayed fractures seems mostly intergranular along the prior austenite grain boundaries.
5. A relationship between susceptibility to delayed fracture and the presence, in these steels, of phases precipitated on the grain boundaries of primary austenite seems to exist. These phases, in low-alloy steels, are probably made up of carbides. The nature of this relationship offers matter for further investigation.
6. In acid environments fractures seem to be mainly due to hydrogen embrittlement.
7. In neutral environments the evidence of various authors is conflicting. An important part could be played in this case by phenomena of the kind of "stress-corrosion" cracking. This is one of the problems for further investigation.

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TABLE I
Composition and Characteristics of Some CrNiMo High-Strength Low-Tempered Steels

Name	Chemical Composition (%)							Mechanical Characteristics		
	C	Si	Mn	Cr	Ni	Mo	V	Altri	Tensile strength (kg/mm ²)	Elongation (%)
V 48	0.48	1.53	0.75	2.94	1.65	0.42	-	-	210	8
V 63	0.63	1.54	0.75	2.91	1.57	0.43	-	-	230	4
Ladish. D6 AC	0.46	0.22	0.75	1.00	0.55	1.00	0.08	-	210	10
Labelle HT	0.45	2.30	1.35	1.40	-	0.40	0.30	-	225	6
Sup. trident	0.55	2.10	0.80	0.90	3.60	0.50	-	-	220	6
4137 (Co)	0.39	1.00	0.70	1.10	-	0.25	0.15	Co 1%	205	6
40NiCrMo7	0.40	0.40	0.65	0.75	1.75	0.25	-	-	-	-
4340*	0.40	0.30	0.70	0.80	1.90	0.25	-	-	190	-
4340 modified*	0.30	0.25	0.90	0.85	1.85	0.45	0.03	-	190	-
HY Tuf*	0.30	1.50	1.40	0.12	1.80	0.35	-	-	160	-
H-350*	0.50	0.25	0.75	0.80	1.85	0.25	-	-	210	-
Trident (300 M)*	0.40	1.60	0.80	0.85	1.85	0.40	0.08	-	210	-
30XCA†	0.30	1.05	0.95	0.95	-	-	-	-	170	-
30XCHA†	0.30	1.05	1.15	1.06	1.60	-	-	-	170	-
643†	0.40	0.85	0.65	0.95	2.75	0.35	-	Ti 0.1% Al 0.1%	200	-

* USA

† USSR

TABLE II
Influence of Ausforming Treatment on the Characteristics of Some 4340 Type Steels

Steels	Deformation			Tensile Strength (kg/mm ²)		Yield Strength (kg/mm ²)		Elongation (%)	
	%	Temperature (°C)	Deformation Method	Ausf.	Usual	Ausf.	Usual	Ausf.	Usual
4340	71	593	Forging	225	193.4	183	158.2	5	10
V 48	90	538	Rolling	309.4	243.3	211	135	9	5
V 63	90	538	Rolling	337.5	235.5	235.5	172.3	8	1
Lad. D6A	71	593	Forging	316.5	211	228.5	165.3	6	10
Labelle HT	65	482	Spinning	262.3	190	247.5	169	5	6
Supertrenic	65	482	Spinning	341	221.5	211	179.3	10	6

TABLE III

Treatments and Properties of Steels Deformed and Tempered after
Conventional Heat Treatment:

Characteristics	4340	Steel	D6 AC Steel
Austenitizing { Temperature ($^{\circ}$ C) Time (min)	830 40	830 40	840 30
Quenching	Oil	Oil	Salt at 175 $^{\circ}$ C
Tempering { Temperature ($^{\circ}$ C) Time (h)	205 1	260 1	205 2 + 2
Ausforming (%)	1	3	0.8
Second Tempering { Temperature ($^{\circ}$ C) Time (h)	205 1	150 1	175 2
Tensile strength R (kg)	207	234	234
Yield strength	207	234	228
Striction (%)	44	35	25
Elongation (%)	6.2	3	3.5

TABLE IV
Composition and Mechanical Characteristics of Some 5% Cr Steels

Chemical Composition

	C%	Si%	Mn%	Cr%	Ni%	Mo%	V%	W%
Vascojet 1000	0.40	—	—	5.00	—	1.30	0.50	—
Potomac A	0.38	0.90	0.34	5.15	0.12	1.26	0.47	0.11
Halcomb 218	0.40	1.05	0.40	5.00	—	1.35	0.50	—

Mechanical Characteristics

	Conventional Quenching and Tempering				Treatment		Properties			
	R (kg/mm ²)	E (kg/mm ²)	A (%)	Σ (%)	Austenitising	Forming	R (kg/mm ²)	E (kg/mm ²)	A (%)	Σ (%)
Vascojet 1000	216	188	7	27	1040°C	480°C/50%	259	220	7	23
Potomac A	192	150	8.5	—	1070°C	480°C/94%	285	277	9	42
Halcomb 218	200	157	4.5	—	—	540°C/32%	225	190	3	—
						480°C/50%	270	210	9	—

TABLE V

Composition and Properties of 18% Ni Maraging Steels

18% Ni Maraging Steel		R = 140 kg/mm ²	R = 175 kg/mm ²		R = 210 kg/mm ²
Composition (%)	Ni	17 - 19	17 - 19		18 - 19
	Ti	0.15-0.25	0.3 - 0.5		0.5 - 0.7
	Al	0.05-0.15	0.05-0.15		0.05-0.15
	Co	8 - 9	7 - 8.5		8.5 - 9.5
	Mo	3.0 - 3.5	4.6 - 5.1		4.7 - 5.2
	Nb	-	-		-
Treatment		480°C - 34	480°C - 34		480°C - 3h Ageing after rolling
			air	vacuum	
Properties in bar shape	E (kg/mm ²)	133-147	166-188	-	207-212
	R (kg/mm ²)	140-154	175-192	-	208-214
	A (%)	14-16	10-12	-	12
	Σ (%)	35-70	48-58	-	60
	Resilience Charpy V (kgm)				
	at 21°C	8.4-15.4	2.5-3.6	3.5-4.0	-
	at 160°C	4.2- 8.4	1.7-2.1	-	-
	Fatigue limit	66	66-70	-	-

TABLE VI

Alloy Element	Lowering of M_s (in $^{\circ}\text{C}$) every 1% alloy element (Steven-Haynes) (1)	Tempering retardation Hardness variation (1) (2)	Rate (Irvine ⁵⁰) (2) (1)
C	474	- 40	tempering still negative
Mn	8	33	0.24
Ni	8	17	0.5 (not certain)
Co	8	small increase	8
Si	20	11	1.8
Cr	0	17	0
W	10		0.9
Mo	17	21	0.9
V	30		probably >1

TABLE VII
Compounds of Intermediate Phases Whose Presence Has Been Noted in Some Martensites

Steels or Alloys	Composition (%)						Type of Intermetallic Precipitate
	C	Cr	Co	Ni	Mo	Different	
17-7PH	0.04	12	10	7	6	Al = 1.20	Fe ₂ Mo Order compounds: Fe-Cr, Ni, Al
	<0.09	17	-		-		
Maraging	<0.03	-	8-9	18		Al = 0.20 Ti = 0.10	Fe ₂ CoNi Ni ₃ Mo
AFC 77	0.15	14.5	13.5	-	5	0.5 V	M ₂₃ C ₆ M = Fe, Mo, Cr

TABLE VIII

Hydrogen Embrittlement Specimens. G110 Maraging Steel

<i>Stress Level (%)</i>	<i>Charging Conditions</i>	<i>Ageing Time (min)</i>	<i>Life (hours)</i>
98	5 min at 20 mA/in ²	10	NF
92	10 min at 20 mA/in ²	10	NF
95	2 h at 60 mA/in ²	10	NF
90	2 h at 60 mA/in ²	10	NF
	7 h at 60 mA/in ²	10	Failed on loading at approx 90%
<i>Note: All stresses given in percentages of 0.1% PS or NTYS</i>			

TABLE IX
Visible Stress Corrosion Cracking in Atmospheric Tests on Commercially Produced Alloys, Nos. 1-7

A. Rayonne Atmosphere						
Alloy Type	Latest Inspection (Days)	Time to Visible Cracking (Days)				
		U-bend	Two-Point Loaded Specimens			
			150 ksi*	200 ksi	250 ksi	300 ksi
18% Ni	514	OK, OK, OK, OK ¹	OK, OK, OK, OK ²	405, 448, 448, OK ²	OK, OK, OK, OK ²	-
18% Ni	514	OK, OK, OK, OK ¹	OK, OK, OK, OK ²	OK, OK, OK, OK ²	OK, OK, OK, OK ²	-
18% Ni	514	OK, OK, OK, OK ¹	OK, OK, OK, OK ²	OK, OK, OK, OK ²	OK, OK, OK, OK ²	-
18% Ni	514	61, 67, OK, OK ¹	OK, OK, OK, OK ²	OK, OK, OK, OK ²	OK, OK, OK, OK ²	481, OK, OK, OK ²
20% Ni	266	22, 53, 266, OK ⁵	22, 22, 22, 22	14, 15, 22, 22	7, 14, 14, 14	-
25% Ni	420	OK, OK, OK, OK ⁶	OK, OK, OK, OK	OK, OK, OK, OK	-	-
4340	49	14, 14, 14, 28	22, 28, 46, 49	14, 14, 14, 18	14, 14, 14, 14	-
B. Kure Beach 80 ft Lot						
18% Ni	491	OK, OK, OK, OK ³	350, 350, 350, OK ⁴	288, 288, 288, OK ⁴	OK, OK, OK, OK ⁴	-
18% Ni	491	OK, OK, OK, OK ³	OK, OK, OK, OK ⁴	OK, OK, OK, OK ⁴	OK, OK, OK, OK ⁴	-
18% Ni	491	OK, OK, OK, OK ³	OK, OK, OK, OK ⁴	OK, OK, OK, OK ⁴	OK, OK, OK, OK ⁴	-
18% Ni	491	155, 345, OK, OK ³	OK, OK, OK, OK ⁴	350, OK, OK, OK ⁴	327, OK, OK, OK ⁴	56, 245, 288, OK ⁴
20% Ni	13	13, 13, 13, 13	13, 13, 13, 13	13, 13	13, 13, 13, 13	-
25% Ni	414	OK, OK, OK, OK	OK, OK, OK, OK	OK, OK, OK, OK	-	-
4340	7	2, 7, 7, 7	7, 7, 7, 7	7, 7, 7, 7	1, 2, 7, 7	-

* 1 ksi = 1000 lb/in²

Note: Superscript numbers indicate the following lengths of exposure in days before removal for micro-examination: (1) 261, (2) 272, (3) 219, (4) 247, (5) 185, (6) 127.

TABLE X
Results of Stress Corrosion Cracking Tests in Sea Water on Commercially Produced Alloys, Nos. 1-7

Alloy No.	Alloy Type	Time to Visible Cracking (Days)			Results of Micro-examination at 218 Days	
		Days in Test	Unprotected U-bends	Cathodically Protected U-bends		Protected at -1.2 volts*
				-0.85 volts*	-1.2 volts*	
1	18% Ni	490	OK, OK ¹	OK, OK	d	OK
2	18% Ni	490	OK, OK ¹	OK, OK	d	-
3	18% Ni	490	OK, OK ¹	6, OK	D	-
4	18% Ni	490	355, OK ¹	9, 29	OK	-
5	20% Ni	461	4, 21	211, 396	-	-
6	25% Ni	413	180, OK	OK, OK	-	-
7	4340	6	6, 6	6, 6	-	-

* Potential against a saturated calomel electrode.

¹ = Removed at 218 days for micro-examination.

d = Shallow microcracks (depth 1-5 mils).

D = Deep microcracks (depth >10 mils).

TABLE XI
Stress Corrosion Tests in 3% Sodium Chloride Solution

Material and Cast No.	Form	Heat Treatment	Applied Stress, (tons/in ²)	Life (hr)	
Maraging steel "110 ton" 07413	¾ in dia	½ hr 830°C AC + 8 hr 450°C	98	2,793	Numerous pits. Fracture transcrystalline with two branch cracks also transcrystalline. No cracking apart from fracture.
Maraging steel "110 ton" 06682	¾ in dia	" " " "	98	933	Transcrystalline fracture. Additional transcrystalline cracks.
Maraging steel "110 ton" VA213	¾ in dia	¾ hr 820°C AC + 3 hr 480°C	98	3,400NF*	
Maraging steel "110 ton" VA213	5 in ² longitudinal	" " " "	98	990	No cracks except fracture, which was inter-granular and unbranched.
Maraging steel "110 ton" VA213	5 in ² transverse	" " " "	98	5	No cracks except fracture, which showed both inter- and trans-granular characteristics and had a few very short branches.
Maraging steel "125 ton" VA275	¾ in dia	" " " "	110	1,371	
Maraging steel "125 ton" VA275	5 in ² longitudinal	" " " "	110	404	No cracks except fracture, which showed both inter- and trans-granular characteristics and was branched.
Maraging steel "125 ton" VA275	5 in ² transverse	" " " "	110	96	No cracks except fracture, which was trans-granular and unbranched.
Rex 539 01960	¾ in dia	1 hr 850°C AC + 1 hr 375°C	92	4,262	No cracking. Ductile failure with necking due to reduced section as a result of corrosion.
En 30B 75973	¾ in dia	1 hr 820°C AC + 1 hr 200°C	65	5,225	Numerous intercrystalline cracks.

* NF = not failed.

TABLE XII

Time to Failure in Boiling 6% NaCl + 1.5% Na₂Cr₂O₇

Heat	Condition	Stress (lb/in ²)	Time (h)
A	ann. + age	150,000	15.6
A	ann. + age	150,000	15.1
B	ann. + age	150,000	42.2
B	ann. + age	150,000	20.9
A	ann.	65,000	No failure*
A	ann.	65,000	No failure*
B	ann.	65,000	No failure*
B	ann.	65,000	No failure*

* Test was stopped after 215 h

TABLE XIII

Time to Failure in 5% Acetic Acid Saturated with H₂S

Heat	Condition	Stress (lb/in ²)	Time (h)
A	ann. + age	150,000	0.9
A	ann. + age	150,000	0.8
B	ann. + age	150,000	0.5
B	ann. + age	150,000	0.4
A	ann.	65,000	11.4
A	ann.	65,000	11.1
B	ann.	65,000	4.9
B	ann.	65,000	3.0

Heat A:C = 0.029%, Heat B:C = 0.004%

TABLE XIV

Effect of Heat Treatment on Resistance of 18% Ni Alloy to Stress Corrosion Cracking

Heat Treatment (°F/time, hr)	Grain Size	Days to Visible Cracking in 3.5% NaCl
CR, 1500/1/4, AC; 900/3, AC	Small	OK*, OK*
CR, 2200/1, WQ; 900/3, AC	Very large	3, 6
CR, 2200/1-1400/24, AC; 900/3, AC	Very large	0.2, 0.6
CR, 2200/1-1400/24, AC; 2200/1, WQ; 900/3, AC	Very large	0.2, 0.8

* Test terminated after 30 days.

CR = Cold rolled WQ = Water quenched AC = Air cooled to room temperature

Note. Centigrade equivalents of Fahrenheit temperatures can be calculated by the following formula: C = (F-32) × 5/9.

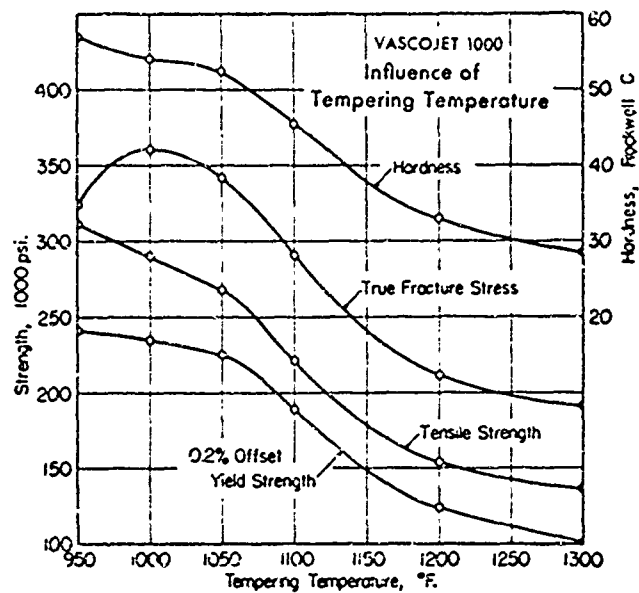
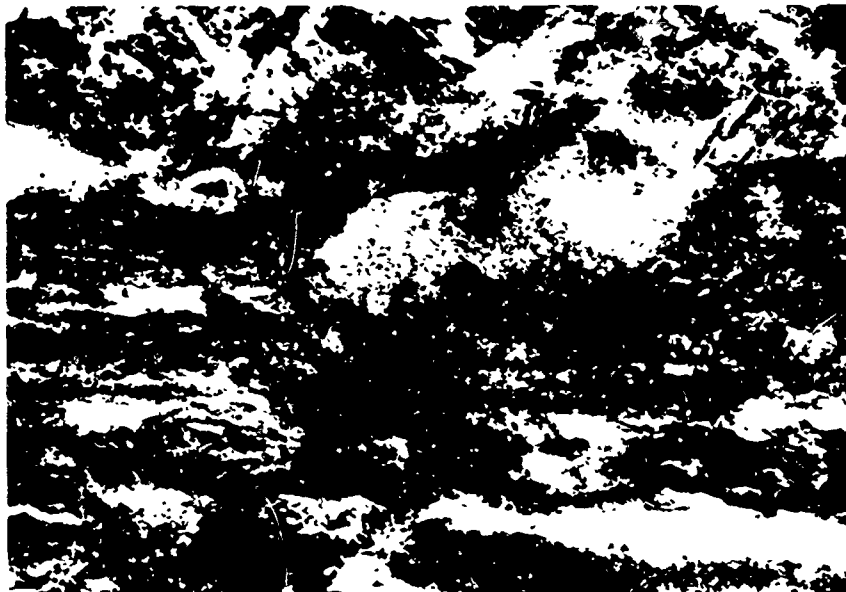


Fig.1 All strength levels from 150,000 – 300,000 lb/in² tensile are attainable in Vascojet 1000 by adjusting the tempering temperature between 950° and 1200°F (Ref. 36)



x 20 000

Fig.2 Extration replica. Segregates of granular and rod-like carbide particles. The other regions contain very fine precipitates visible with greater amplification (Ref. 35)

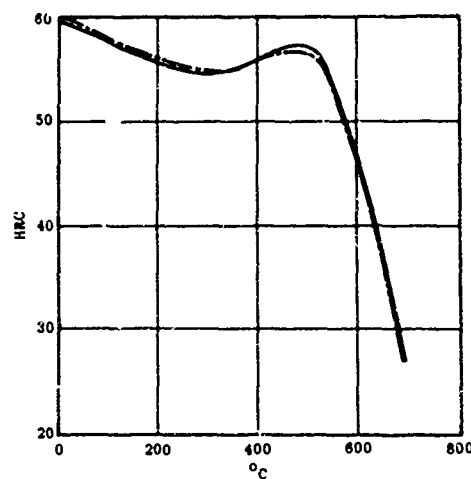


Fig.3(a) The effect of tempering temperature on the hardness of steel No.82. 5% CrMoV.
Austenising temperature (Ref.35)

———— 1030°C }
- - - - - 1100°C } tempering time 2 hr

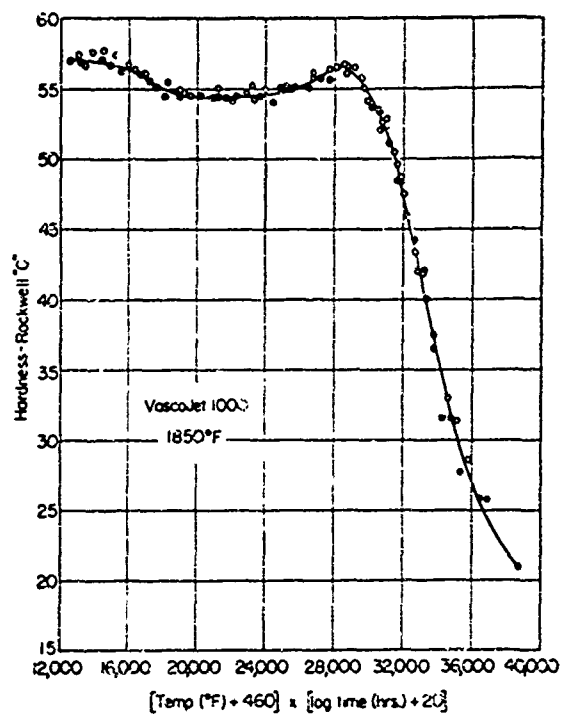


Fig.3(b) Master tempering curve for Vascojet 1000. Allowable operating temperatures and times for maintaining stable elevated temperature properties can be precisely calculated from formula shown on horizontal axis (Ref.36)

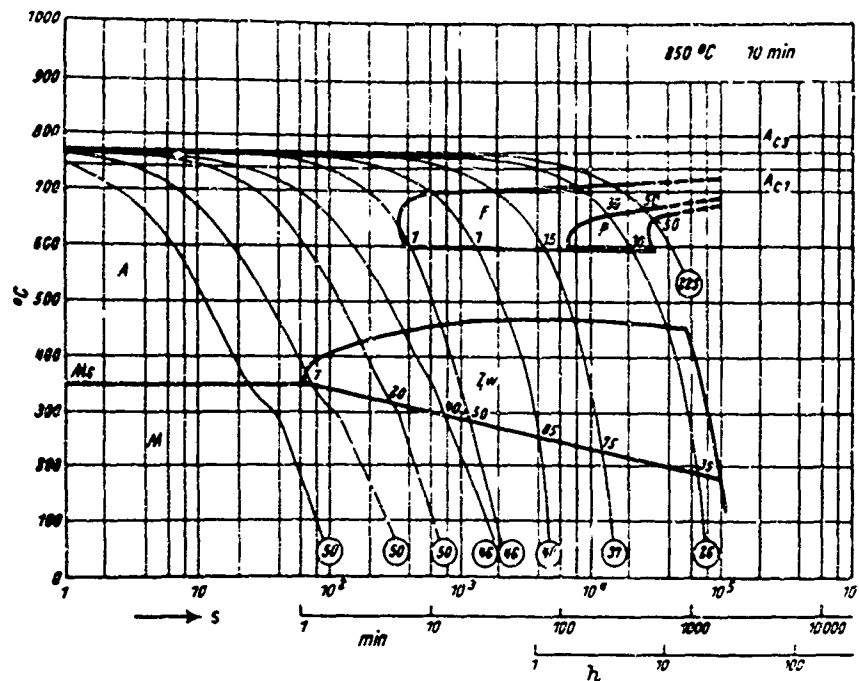


Fig. 4 Continuous cooling transformation diagram for steel No. 102, approximate En 25 (Ref. 35)

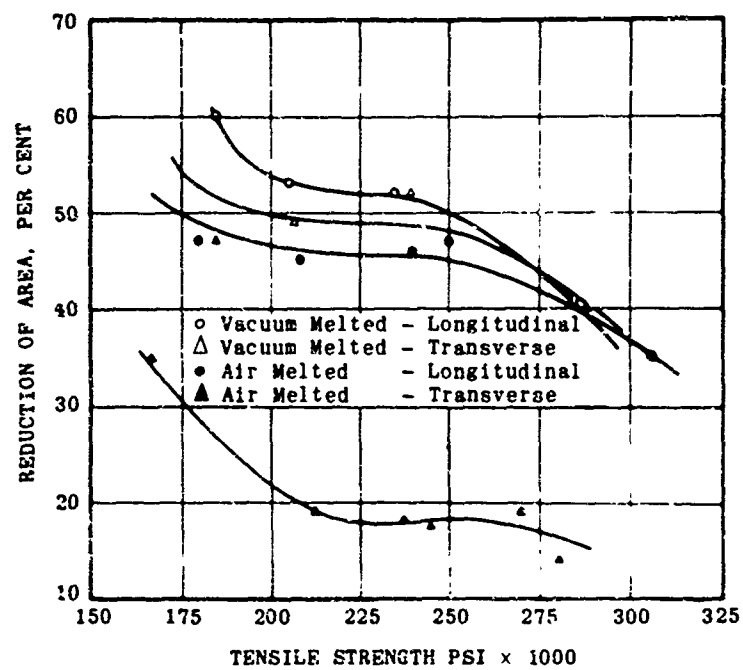


Fig. 5 Ductility of vacuum melted and air melted 4340 steel as a function of tensile strength (Ref. 1)

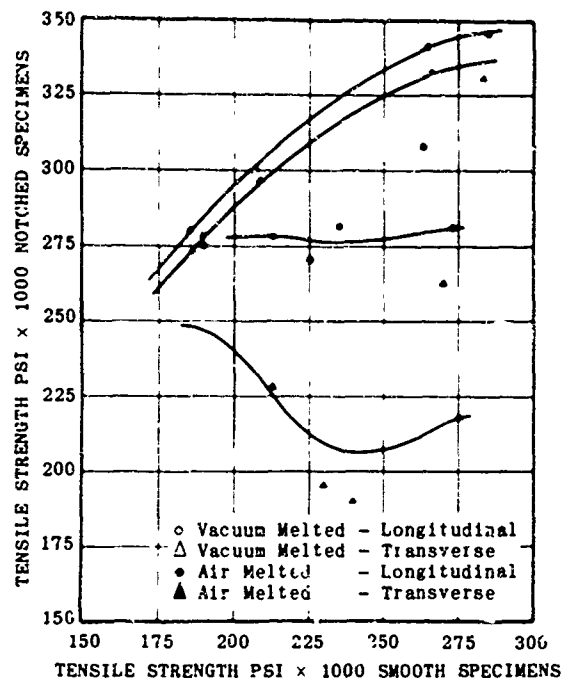


Fig. 6 Notch strength of vacuum melted and air melted 4340 steel as a function of tensile strength (Ref.1)

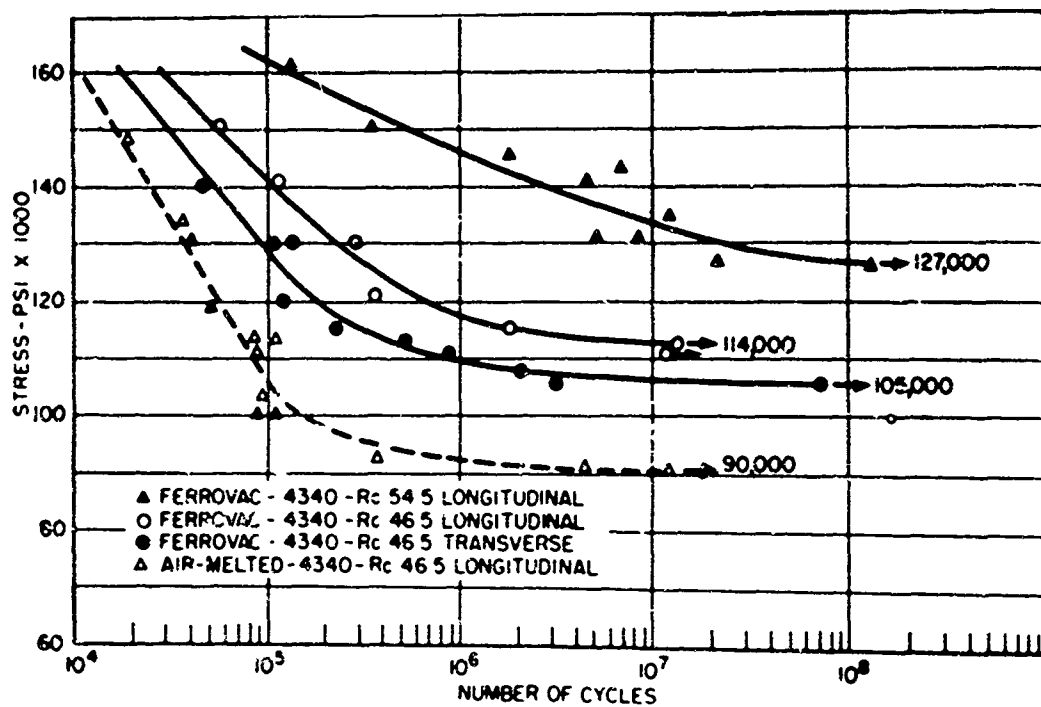


Fig 7 Rotating beam fatigue behaviour of Ferrovac 4340 vacuum or air melted (Ref.1)

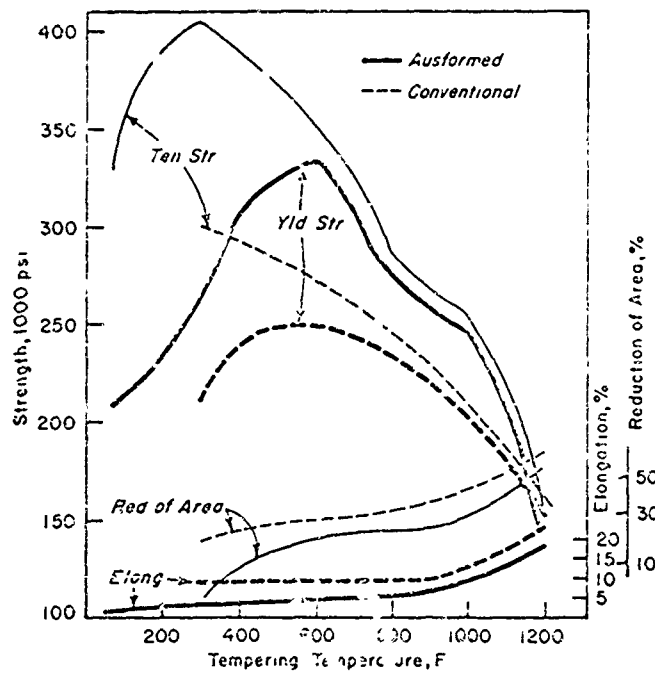


Fig.8 Mechanical properties of D6A steel: comparison of ausforming with conventional heat treatment (Ref.33)

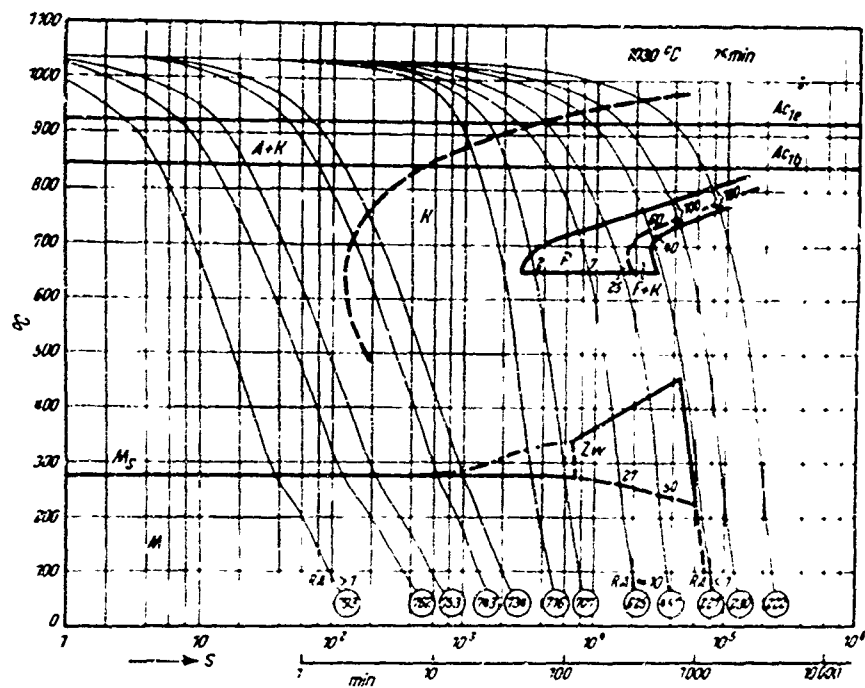


Fig.9 Continuous cooling transformation diagram for steel No.82, 5% CrMoV (Ref 35)

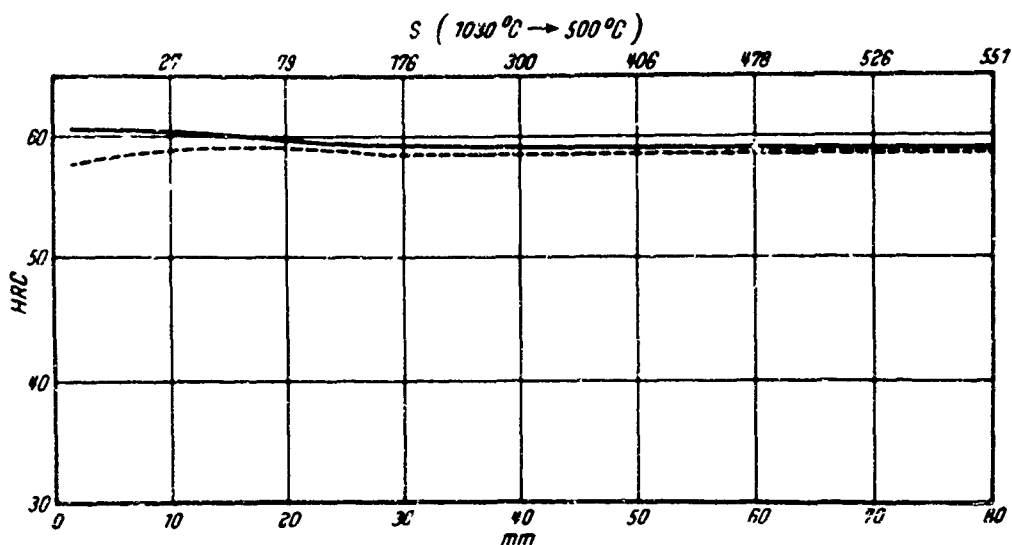


Fig. 10 Hardness HRC plotted against distance from the end, of an end quench test specimen of 18.5 mm diameter, 100 mm length, for steel No. 82. Austenising temperature 1030°C (Ref. 35)

— — — — — untempered
 - - - - - tempered at 500°C

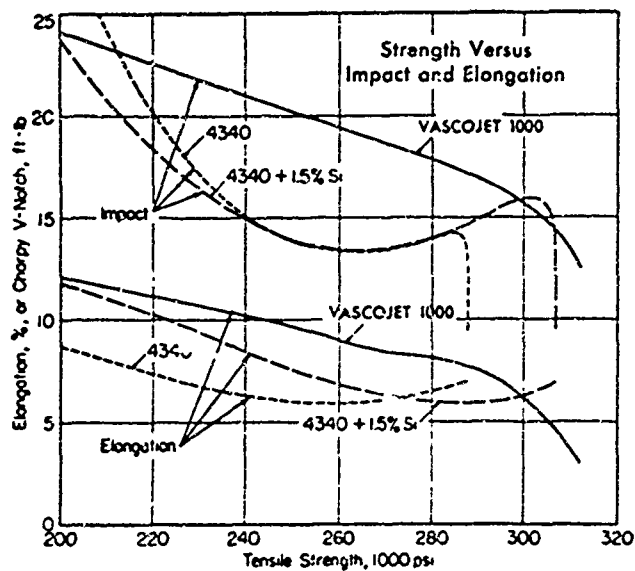


Fig. 11 Impact toughness and ductility of the 5% chromium steel are 20-25% higher than 4340 types at high-strength levels. With no embrittlement range or retained austenite, they vary proportionately with tensile strength (Ref. 36)

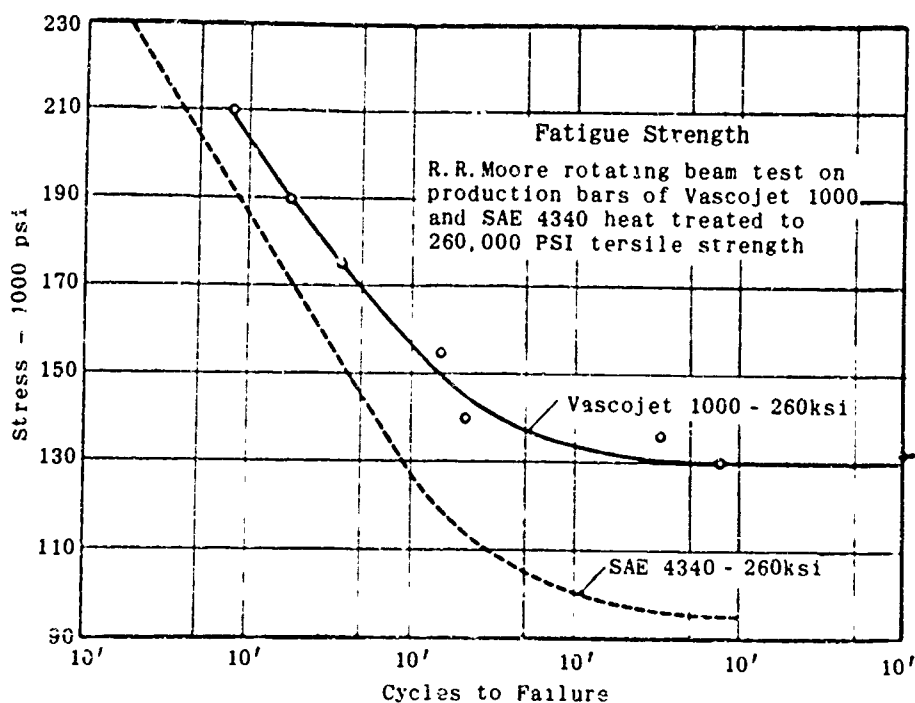


Fig. 12 From 8000-100,000,000 cycles, the fatigue strength of Vascojet 1000 is 10-35% greater than any air-melted material previously reported (Ref. 36)

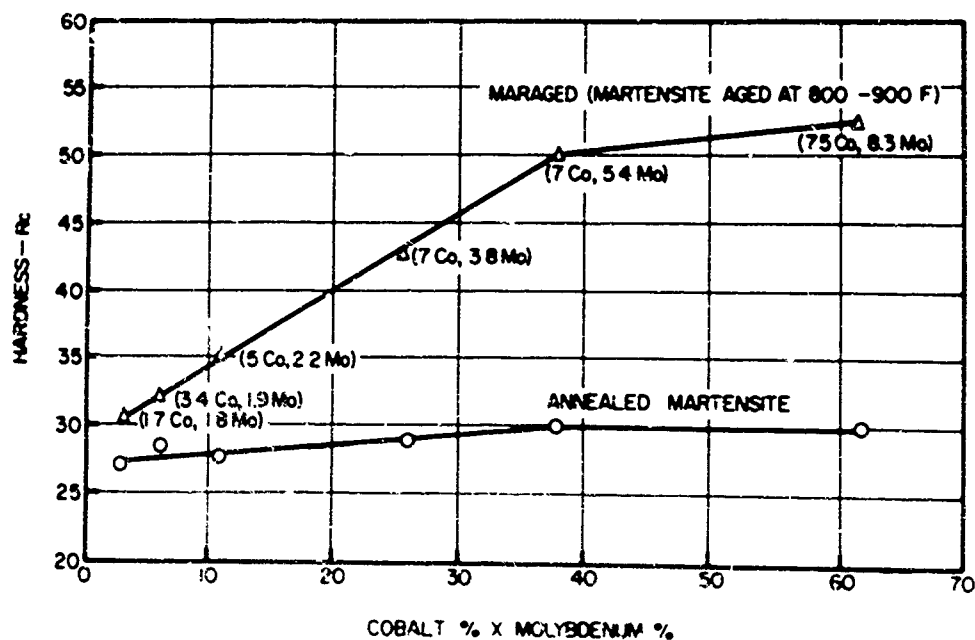


Fig. 13 Effect of product of cobalt X molybdenum on maximum hardness of 200-g melts of 18.5 to 20.1 NiFe alloys. Solution annealed 1 hr at 1600°F, air cooled; maraged 3 to 10 hr at 800 to 900°F (Ref. 22)

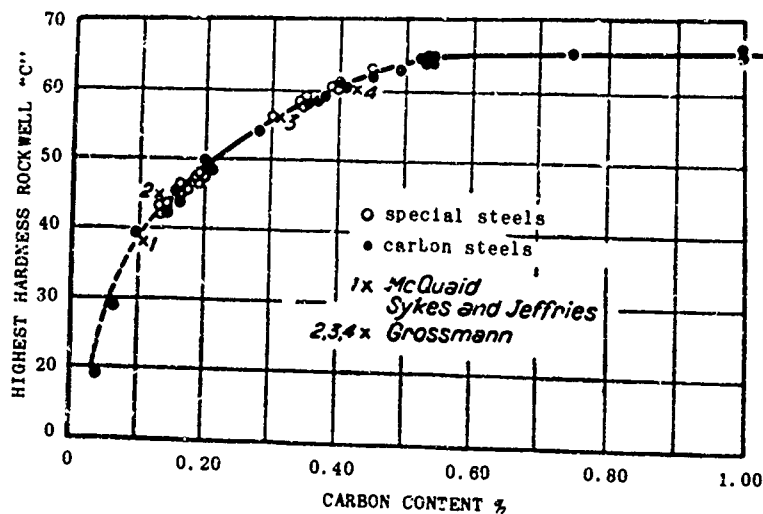


Fig. 14 Highest hardness of martensite as a function of carbon content

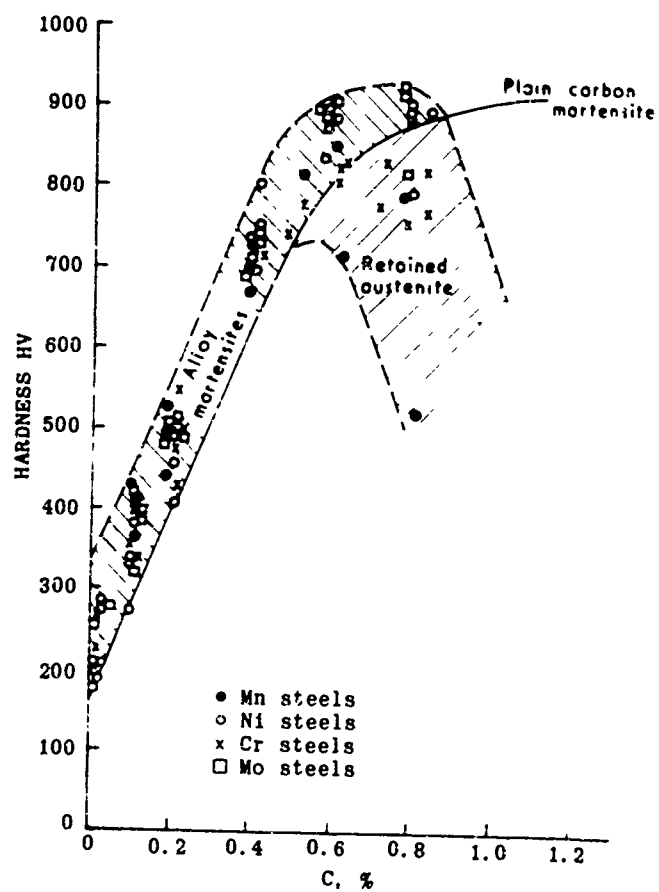


Fig. 15 Effect of alloying elements on the hardness of martensite

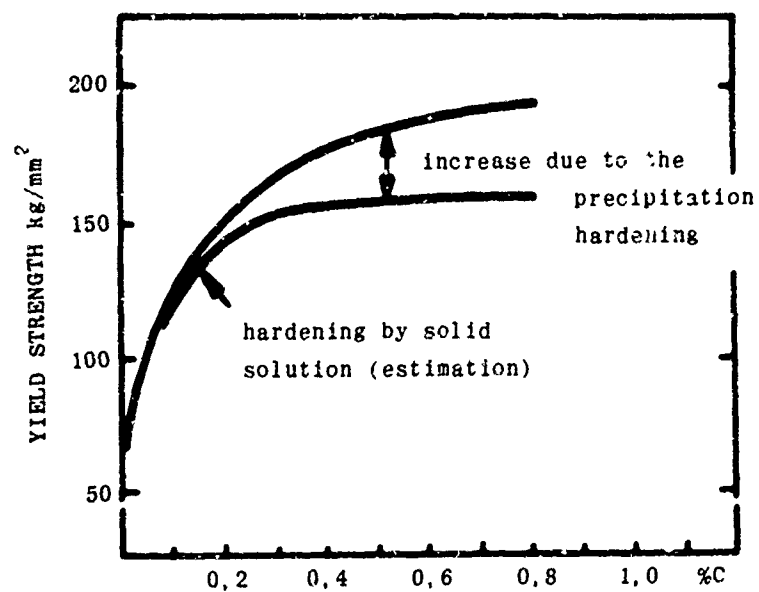


Fig. 16 Hardening by solid solution and by precipitation in a martensite with a variable carbon content

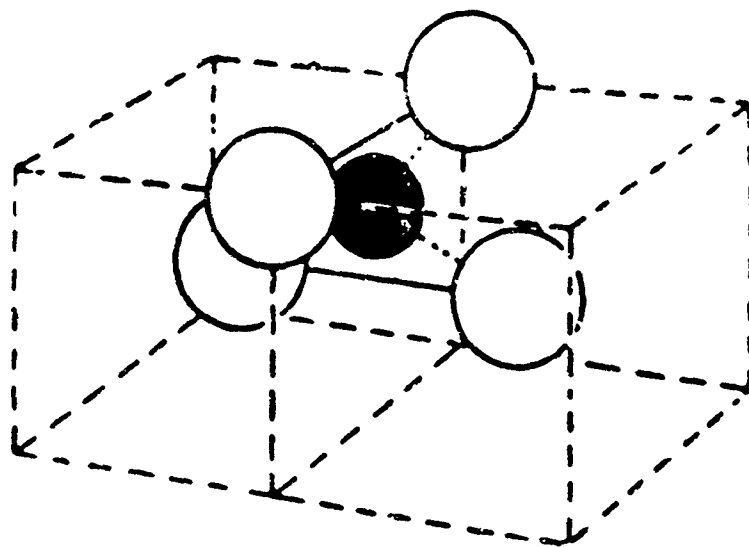


Fig. 17 Probable position of carbon atom in α iron

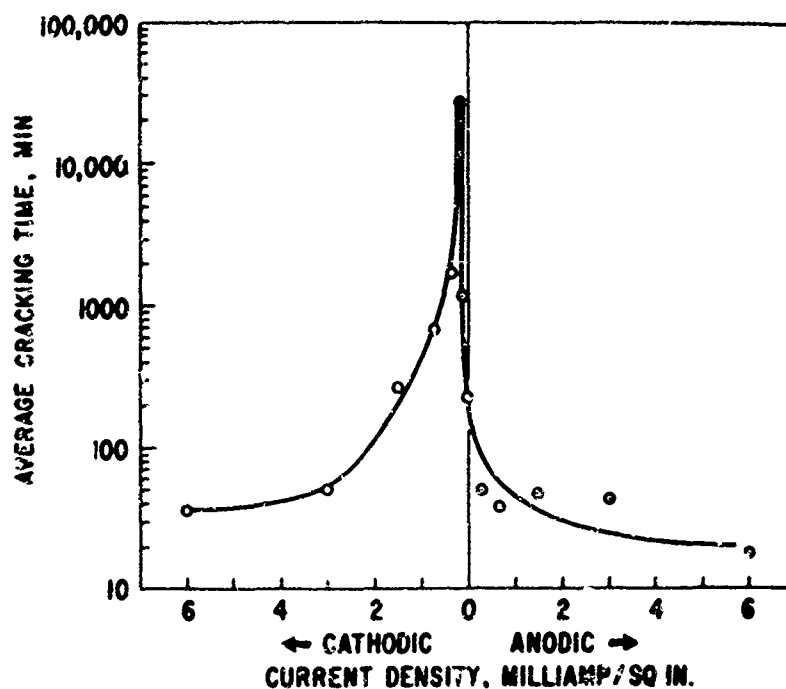


Fig. 18 Effect of applied current on cracking time, USS 12 MoV stainless steel in aerated 3% NaCl solution

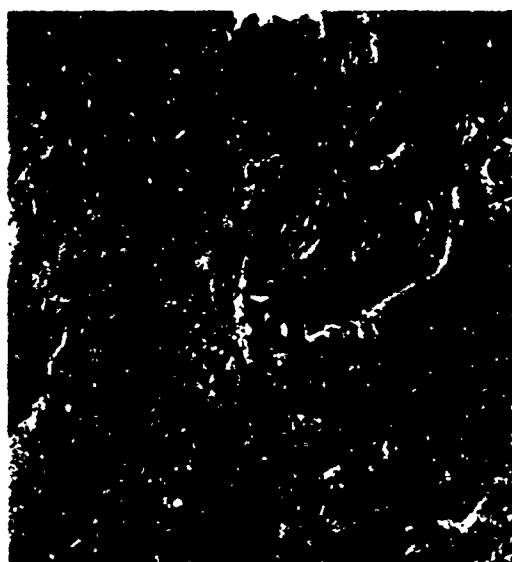


Fig. 19 Appearance of stress corrosion crack in Airsteel X 200. Super picral etch, approximately 290 X



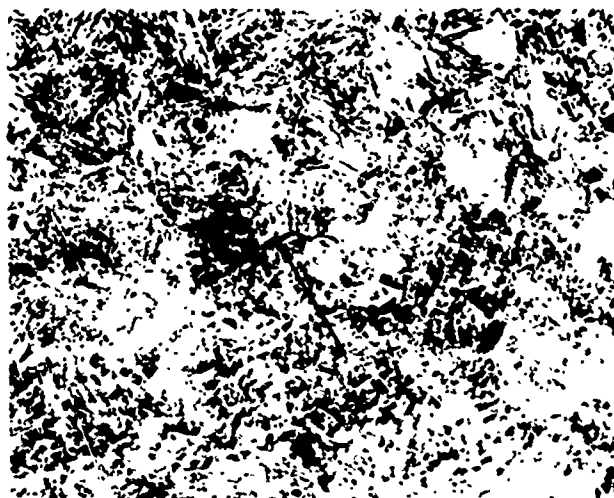
x 2000

Fig. 20 Intergranular fracture area, stress corrosion failure, specimen tempered 450°C



x 3000

Fig. 21 Mixed fracture area, stress corrosion failure, specimen tempered 230°C



x 800

Fig. 22 A small crack emanating from a pit on the tensile surface of a stress corrosion specimen. Light Nital etch

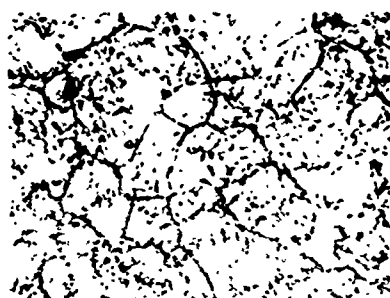


(a) Zephiran chloride. 1000X

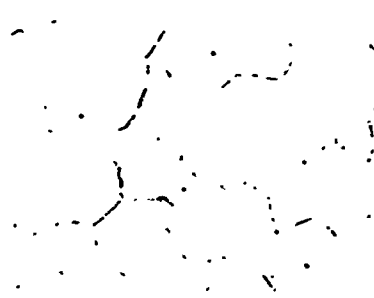


(b) Repolished. 1000X

Fig. 23 Microstructure of 4340 alloy steel at a yield strength of 222.4 ksi*, showing form and distribution of carbide precipitate



(a) Zephiran chloride. 1000X



(b) Repolished. 1000X

Fig. 24 Microstructure of 4340 alloy steel at a yield strength of 194.1 ksi*, showing form and distribution of carbide precipitate

* 1 ksi = 1000 lb/in²



x 890

Fig. 25 Micrograph showing the beginning of fracture at an inclusion site slightly away from the fracture surface

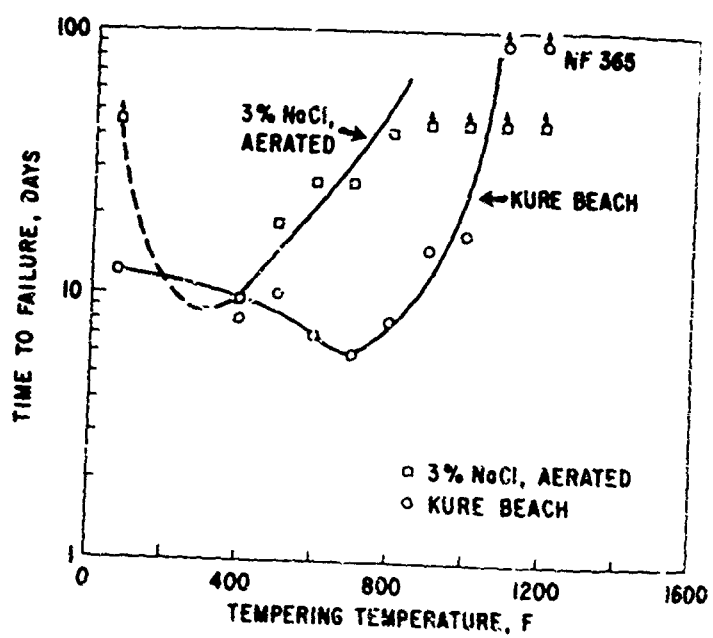


Fig. 26 Effect of tempering temperature on stress corrosion of A1rsteel X 200

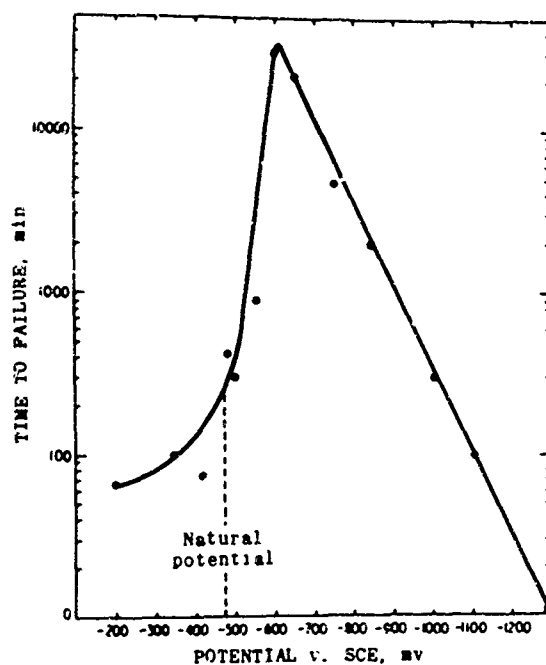


Fig. 27 Effect of impressed potential on time to failure under sustained load in 3% NaCl

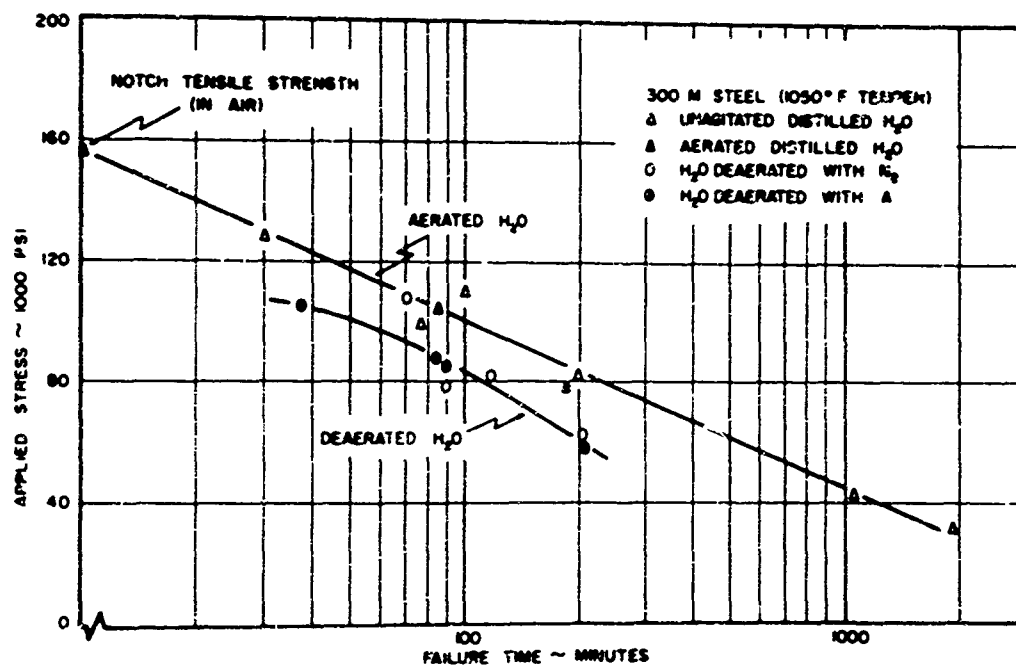


Fig. 28 Influence of the oxygen content of distilled water on the delayed failure characteristics of 300 M steel, 220,000 lb/in² strength level, at 68°F

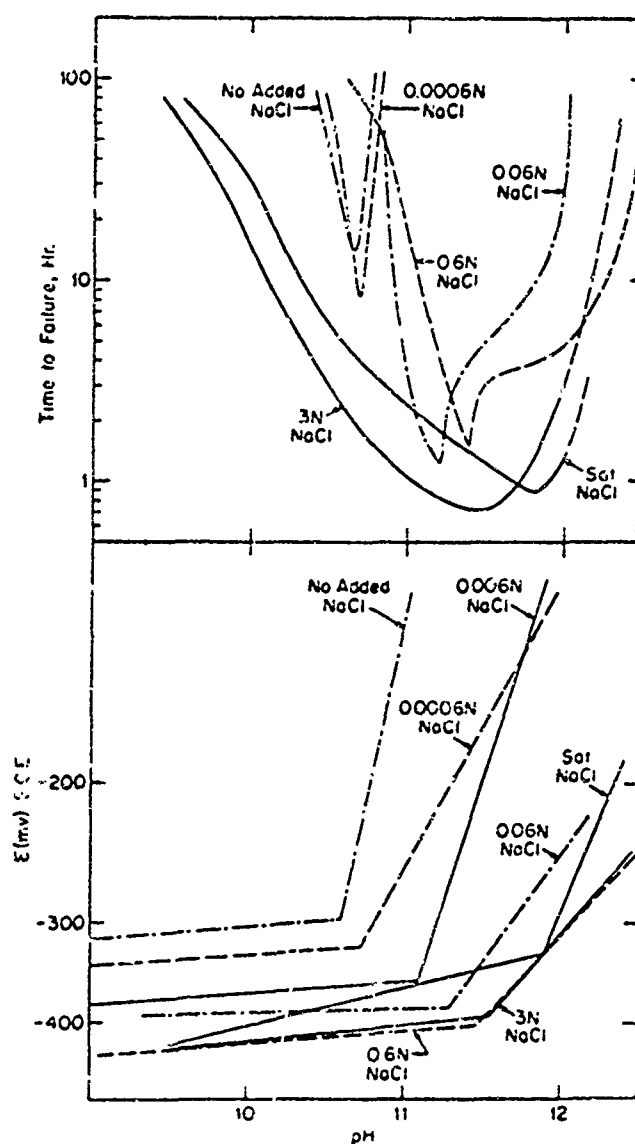


Fig.29 Relation between time-to-failure of 18 Ni maraging steel immersed in a series of environments from deionized water saturated with NaCl to solutions containing no added NaCl as a function of pH. The lower figure illustrates changes of electrode potential for the same range of environments as a function of pH

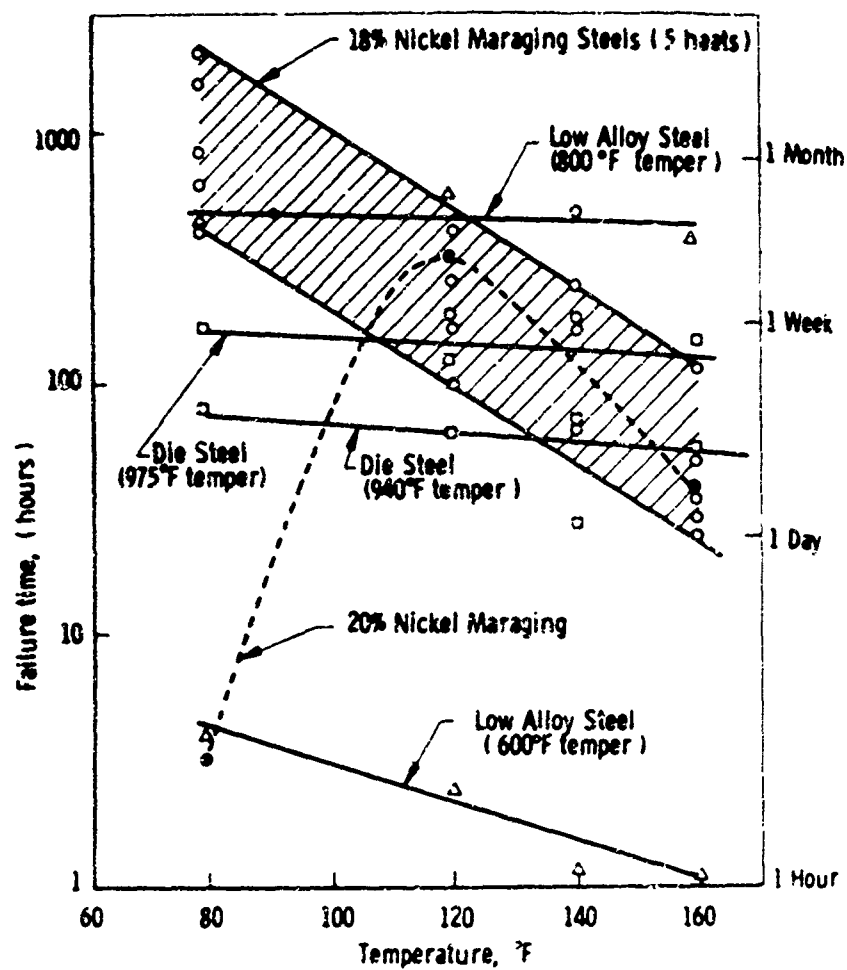
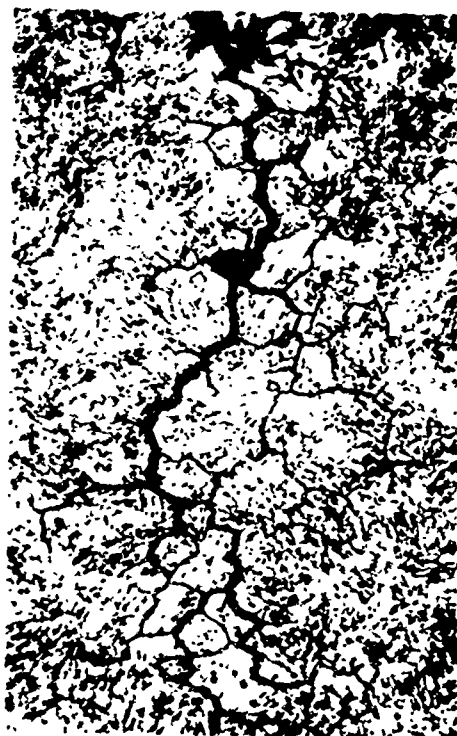


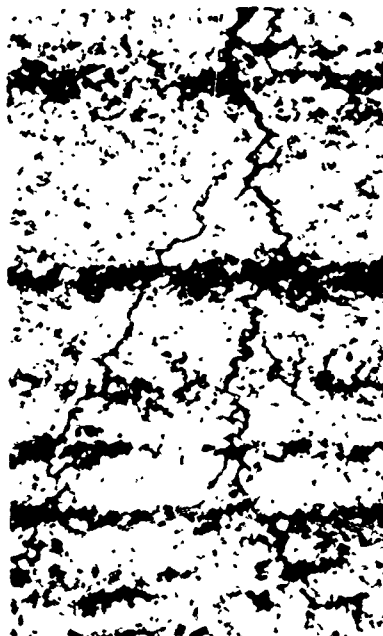
Fig. 30 Effect of temperature in distilled water. These U-bend tests show that the time-to-failure of the maraging steels in temperatures above ambient decreases more rapidly than with the low-alloy or hot-work die steels



x 500

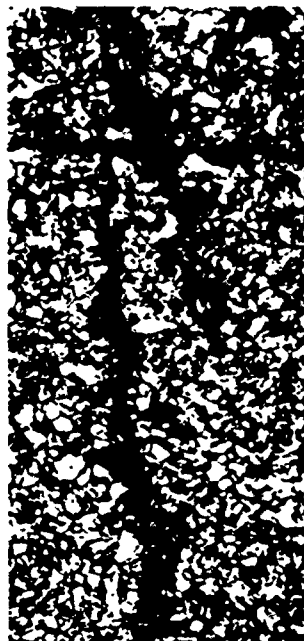
Fig. 31 Deep intergranular microcrack (18% Ni, 200 ksi*) exposed as two-point-loaded specimen at 200 ksi for 247 days in 80 ft lot at Kuré Beach.
Etchant: modified Fry's reagent

* 1 ksi = 1000 lb/in²



x 500

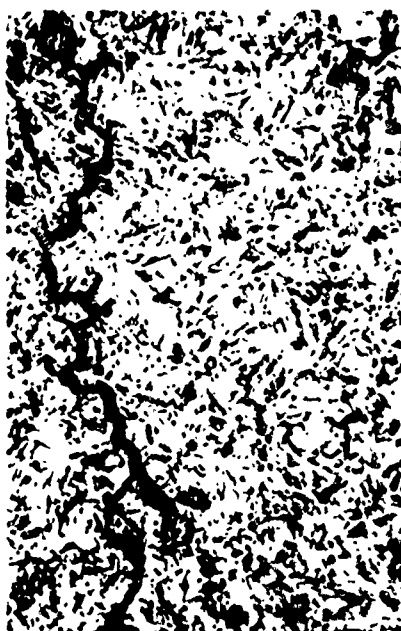
Fig. 32 Two-point-loaded specimen (18% Ni, 250 ksi) exposed to Bayonne atmosphere 272 days, load 200 ksi*. Etchant: 2% Nital. Stress corrosion cracks



x 500

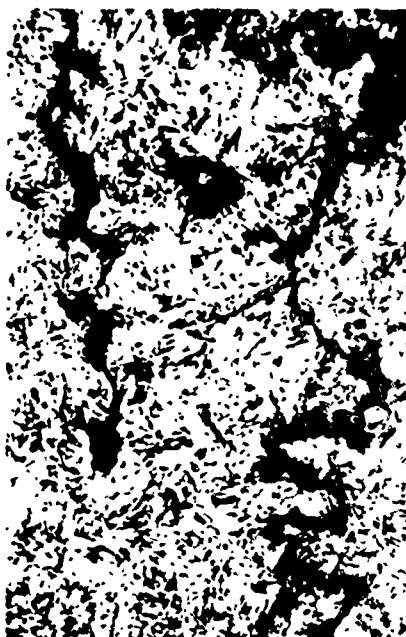
Fig. 33 Cathodically protected U-bend (18% Ni, 250 ksi*) exposed to sea water at -1.2V for 14 days. Etchant: 2% Nital. Cracks are hydrogen cracks

* 1 ksi = 1000 lb/in²



x 500

Fig.34 U-bend of AISI 4340 exposed to sea water 6 days. No cathodic protection.
Etchant: 2% Nital. Stress corrosion cracks



x 500

Fig.35 Cathodically protected U-bend of AISI 4340 exposed to sea water at -1.2V for
6 days. Etchant: 2% Nital. Hydrogen cracks

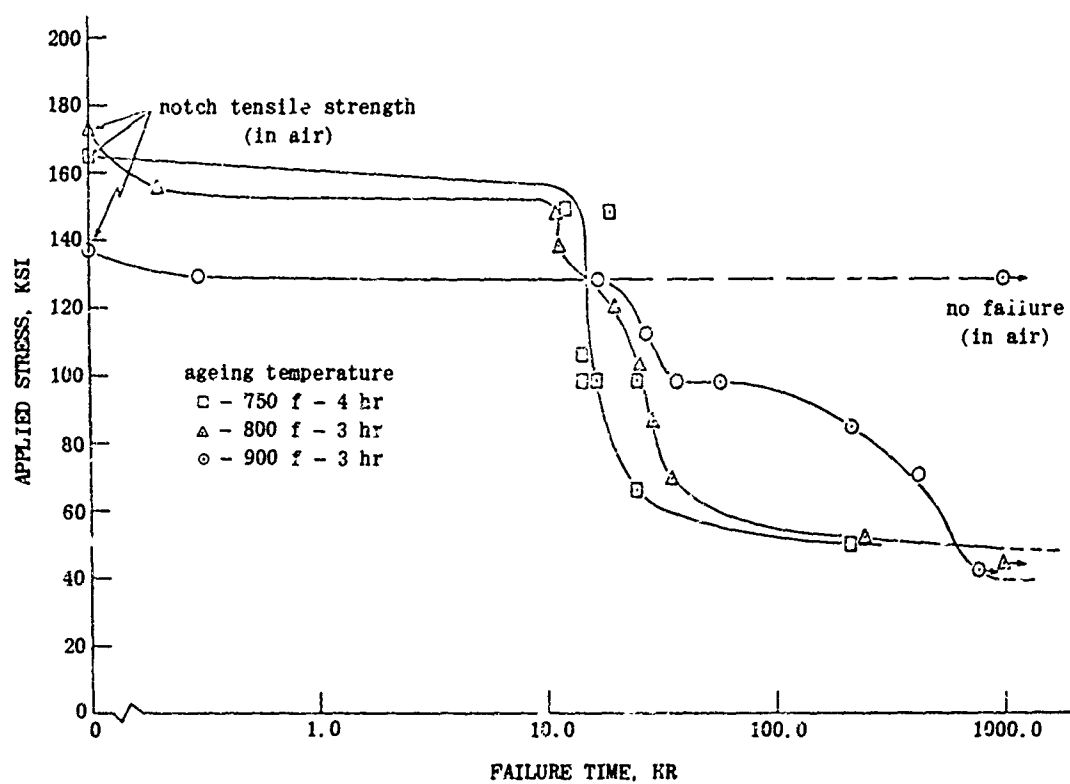


Fig.36 Delayed failure characteristics in distilled water at 70°F

DISCUSSION ON PAPER BY PROF. MATTEOLI AND DR SONGA

Concerning the susceptibility of different steels to SCC, Dr E.H. Phelps showed a summary of data on a large number of heat treated high tensile steels. The steels had been exposed as unprotected bent beams stressed at 75% yield strength eight feet from the sea at Kuré beach. All those steels with a tensile strength less than 180 ksi (80 tons/in²) survived for a long time and were finally withdrawn because of general corrosion. Of the steels with yield strength in the range 180 to 210 ksi (80 to 94 tons/in²), some failed and some did not. All those stronger than 210 ksi (94 tons/in²) failed by SCC. 18 Ni maraging steels fell into the same pattern, except that those which failed did so after a time much longer than that of conventional steels of the same strength.

Dr Phelps then referred to electrochemical polarisation experiments undertaken to distinguish between the two mechanisms of SCC failure of steel, viz. Active Path Corrosion and Hydrogen Embrittlement. Eight types of result were possible, as shown in Figure A-1. It should be noted in this figure that curve A represented the case where only hydrogen embrittlement was obtained, whereas curve B showed only active path corrosion. Both processes were shown in curves C and D with the significant difference that curve D had an open zone where no failure occurred. This meant that there was a range of cathodic potentials in which the steel could be cathodically protected without introducing enough hydrogen to cause hydrogen embrittlement. Where both anodic and cathodic polarisation shortened the cracking time, as in curve E, it was not possible to determine which mechanism prevailed without applied current.

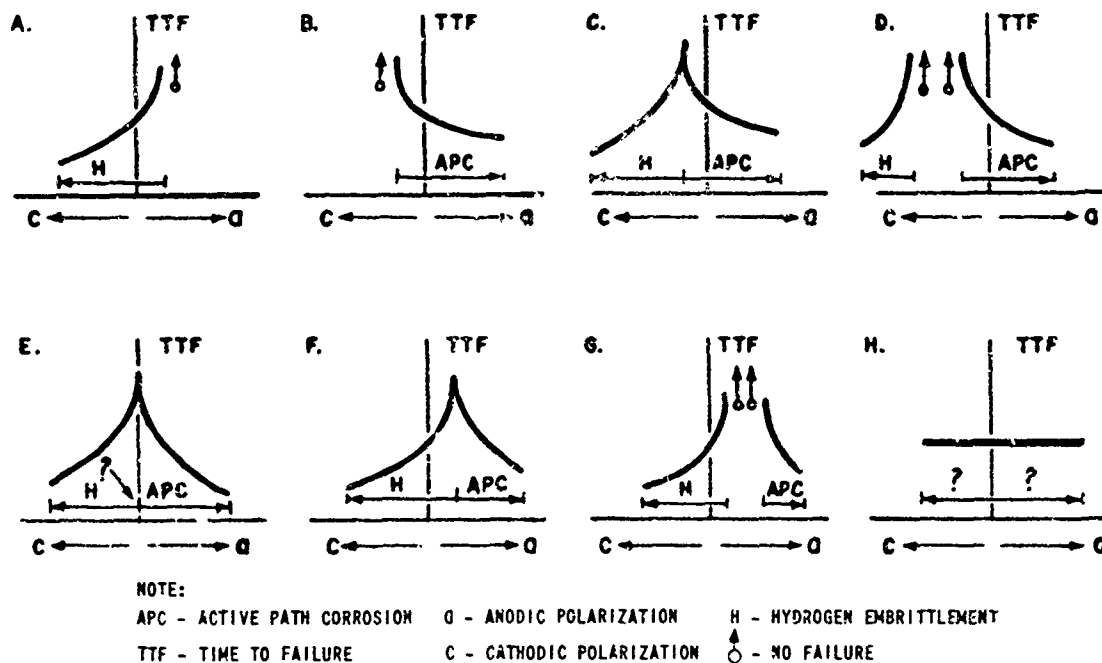


Fig. A-1 Possible relationships between time-to-failure and anodic or cathodic polarisation

Curves F and G might be expected in acid solutions when the corrosion potential was anodic to the reversible hydrogen potential. With curve H neither anodic nor cathodic polarisation had any effect on cracking time. A possible explanation was that a hydrogen embrittlement mechanism was involved, but that the mechanism by which hydrogen entered the steel was not electrochemical. Except for curve G, all the curves had been obtained experimentally.

Mr. B. B. Rosenbaum described a new steel developed for ship and submarine hulls which might also find use for rocket motors. Designated HY 130, it contained 5 Ni, 1 Cr, 0.8 Mo, 0.1 C and 1 V and had a yield strength of 130 ksi (58 tons/in²). The toughness was very high. Slow reverse bend fatigue tests and stress corrosion tests under bending had been made on welded slabs two feet square, one inch thick. Resistance to SCC was very high even in the presence of cracks, and the corrosion fatigue properties were very good.

NATIONAL SURVEYS OF WORK ON STRESS CORROSION CRACKING

NATIONAL SURVEYS OF WORK ON STRESS CORROSION CRACKING

Each Member Country was asked to report on its current research and development work on stress corrosion cracking. The following countries made reports:

<i>Canada</i>	Dr G.J.Biefer, Department of Energy, Mines and Resources, Ottawa.
<i>France</i>	Prof. P.Lacombe, Ecole des Mines et Faculté des Sciences d'Orsay, Paris.
<i>Germany</i>	Prof. Dr-Ing. L.Graf, Max Planck Institute, Stuttgart.
<i>Italy</i>	(i) Aluminium alloys, Dr E. di Russo, Istituto Sperimentale dei Metalli Leggeri, Milan. (ii) Other metals, Colonel A.Griselli, Ministero Difesa Aeronautica, Rome.
<i>Norway</i>	M.A.Winfeldt, Central Institute for Industrial Research, Blindern, Oslo.
<i>United Kingdom</i>	Mr H.Brooks, Royal Aircraft Establishment, Farnborough, Hants.
<i>USA</i>	Mr W.K.Boyd, Battelle Memorial Institute, Columbus, Ohio.

Denmark, Greece and Portugal had no work to report, and *Belgium, the Netherlands and Turkey* made no report.

The national surveys are summarised by the Editor below under the headings Aluminium Alloys, Steels, and Titanium Alloys, followed by further notes where appropriate on the national effort. The very large programme in the USA tends to overshadow the work in other countries; inevitably the smaller effort in other countries has been reported in greater detail.

1. ALUMINIUM ALLOYS

1.1 USA

The problem of stress corrosion cracking in aluminium alloys is not new. Work has been in progress for some time to determine the mechanism of this phenomenon, however, it is still not completely understood. None of the basic theories proposed satisfactorily rationalises all of the experimental evidence. On the other hand, it is generally accepted that the mechanism of cracking is related to a tensile stress-induced electrochemical reaction. More recent modifications of this theory have

involved strain-induced hydrogen absorption at mechanically weak grain-boundary zones which reduce the energy of activation for the corrosion of these zones. Such a mechanism would explain why materials susceptible to intergranular stress-corrosion cracking are not necessarily susceptible to intergranular corrosion.

Because of the electrochemical nature of stress-corrosion cracking, research has centered on environmental and metallurgical conditions which are known to be important in more commonly studied types of corrosion. Combinations of cold rolling and artificial ageing have been found to be of benefit in some alloys, as have special heat treatments where quench temperatures are carefully controlled. In general, such studies have provided more fruitful results than alloying with say silver. Results in this country with silver additions have been disappointing.

The fact that aluminium alloys are most susceptible to stress-corrosion cracking when stressed in tension perpendicular to the rolling or forging plane is generally attributed to grain shape, although in thick sections variations in cooling rate may introduce other metallurgical variables which are contributing factors. Preferred orientation studies have indicated a variation in the orientation of crystallographic planes through the thickness of some materials and therefore a difference in stress-corrosion-cracking susceptibility. On the other hand, little correlation has been found between susceptibility and the variation in mechanical properties observed through the material thickness.

Shot peening to reduce surface tensile stresses is used extensively to prevent initiation of stress-corrosion cracks.

Current research involves the study of a number of factors, namely:

1. The susceptibility to stress-corrosion cracking as a function of:
 - (a) directional effects of grain orientation
 - (b) dislocation environment interaction
 - (c) cathodic processes which promote hydrogen entry into the material
 - (d) alloy composition, e.g., silver additions
 - (e) temper conditions.
2. The development of valid rapid stress-corrosion tests, which can be used to evaluate all types of aluminium alloys and tempers.
3. The development of organic coatings and other techniques specifically designed to improve performance of aluminium structures in service environments.
4. The development of techniques for the detection of stress-corrosion cracking in aluminium alloys.

Those alloy systems receiving the most study, from the standpoint of stress-corrosion cracking, are the high-strength aluminium-copper and aluminium-magnesium-zinc series.

Laboratories where research is in progress are listed in Table I on page 19.

1.2 France

Most of the work in France is carried out by the Services Techniques de l'Aéronautique and by manufacturers of aircraft such as Sud-Aviation and of metals such as Pechiney.

A. Systematic studies

- (i) *Standard corrodent* - Most laboratories in France have adopted the STA formula A₃ which specifies a 3% solution of sodium chloride buffered with boric acid or sodium carbonate to a pH between 8.0 and 8.2; unbuffered media tended to develop an alkalinity which modifies the surface oxide film on the metal.

- (ii) *Test procedure*

- (a) *Sorting tests.* Simple specimens are used which can be cut in the short transverse direction from test parts of not too great a thickness. Tests are made at either constant strain or constant stress.
 - (b) *Systematic tests.* These are more precise and more reproducible. They are made in uniaxial tension on plane or centre notched specimens stressed in a proving ring. Scatter of results can be controlled by the use of a single level of stress of 75 to 80% of the 0.2% proof stress.

Great care is taken in the preparation of the specimens and of the surfaces prior to immersion. Machining must not leave visible traces, and is followed only by degreasing; chemical and electrolytic pickling are avoided so as not to change the nature of the passive oxide film.

It seems more and more certain that only axial tension tests allow quantitative interpretation with minimum scatter of results. It is essential also to conduct parallel corrosion tests without stress under the same conditions. The factor of acceleration due to stress is then

given by the formula $f\% = 100 \times \frac{RT\% - RN\%}{RT\%}$ where RT and RN are the losses

of tensile strength caused respectively by corrosion under stress, and stress-free corrosion of the same duration. Unless this factor is positive one cannot consider the alloy to be susceptible to stress corrosion.

- (iii) *Metallurgical investigations* - The results given below are taken from the work of A. Guilhaudis and Mlle Petrequin at the Pechiney Co. Laboratories, formerly at Chambéry and now at Voreppe.

- (a) *Aluminium magnesium alloys.* For contents of magnesium less than 7%, the purity of the aluminium base (A9, A7, or A5) does not significantly alter the results of stress corrosion tests. Although stress corrosion life decreases with increase in content of magnesium, parallel corrosion tests without stress lead to an accelerating factor of less than 10%, so that one cannot properly speak of any susceptibility to stress corrosion, at least in the salt water medium used.
 - (b) *Aluminium-zinc-magnesium alloys.* The temperature of ageing is critical. Thus, alloy AZ5G3 aged for 120 hr at 90°C is very susceptible, but aged for 24 hr at 150°C is only slightly susceptible.

Alloy AZ4G3 is much more susceptible to corrosion than AZ5G. It has been established that increase in magnesium content above 1.5% causes a catastrophic increase in susceptibility to stress corrosion, due, apparently, for high magnesium contents, to a loss of cohesion at the grain boundaries.

Alloy AZ5GU has been the subject of fundamental researches as described in Section B below. These researches, based on the application of double artificial ageing treatments to alloys aged at room temperature, constitute a new approach to the study of the fundamentals of stress corrosion.

- (c) *Aluminum copper alloys.* Systematic studies are in hand. Tests have shown that the susceptibility to stress corrosion of alloy AU4G1 is much reduced by treatment for 20 hr at 180°C.

B. Fundamental research

This account will be limited to a typical example of fundamental research carried out over the past two or three years at the Pechiney Co. by Develay, Adenis and Guilhaudis. The principal results were presented to the October, 1966, Symposium of the Société Française de Métallurgie.

This research is concerned with the effects of different ageing temperatures and durations on AZ5GU, and its novelty lies in the combination of determination of mechanical properties with investigation by dilatometry, X-ray diffraction, microscopy and electron diffraction. The two latter methods have been especially used to identify the different phases appearing during ageing. These phases, revealed by electron microdiffraction on thin films, have an influence on the susceptibility to corrosion of the alloy which can be seen directly by submitting the thin film to corrosion. Examination of corroded thin films in the electron microscope at X20,000 reveals the type of transgranular or intergranular attack. The study had been inspired by the work of Gruhl and Cordier who had investigated the effect of a second ageing on AZ5GU solution heat treated and aged for 24 hr at 120°C; on further ageing at 180°C, tensile properties fell during the first five minutes, then rose to a maximum after about 2 hr, then fell again (over-ageing).

The Pechiney workers studied systematically the effects of second ageing for various durations up to 20 hr in the range 165 to 190°C. The change in mechanical properties was to be associated with a disappearance of the first transition precipitate form during the first ageing at the lower temperature, and its replacement by phase M¹ of precipitated MgZn₂, first as platelets, then in massive form, then passing to globular form and finally transforming to the M phase. The phase changes were correlated with the change in mode of corrosion from transgranular to intergranular, and the final decrease in susceptibility with overageing.

It was concluded that the susceptibility of AZ5GU to intergranular corrosion is due to the presence of supersaturated zones at the grain boundaries. The fall in susceptibility caused by overageing is ascribed to the impoverishment of these zones by diffusion of alloying elements to the grain boundaries.

The following general conclusions were drawn:

- (a) In aluminium alloys, dislocation pile-ups at grain boundaries are not observed, probably because the high stacking fault energy (280 erg/cm^2) allows easy cross slip. The proposal by Robertson and Tetelmann that crack propagation is caused by dislocation pile-ups at grain boundaries seems invalid for aluminium alloys. The mechanism is more likely purely electrochemical, due to differences in composition between matrix and grain boundaries.
- (b) Optimum mechanical properties are associated with very fine homogenous precipitates of radius of a few hundred Angstrom units. These precipitates are visible only in the electron microscope, and are very difficult to identify. Many of the secondary precipitates formed from minor elements (Fe, Cr, Ti etc.) have not been identified and their structure and composition are not known with certainty. This is an important limitation in current research.

1.3 Germany

P. Brenner, W. Gruhl and H. Cordier are investigating the stress corrosion properties of Al5Zn3.3Mg type alloy at the Vereinigten Leichtmetallwerke Laboratories in Bonn. Tests under constant stress have revealed an exponential relation between stress and life, with a threshold below which stress corrosion does not occur. The life is reduced by 5% for every 1°C rise in temperature. The activation energy for the stress corrosion process is equal to that for vacancy migration in aluminium. Tests in various corrosive media revealed no correlation between surface corrosion and stress corrosion.

The increase in life with increased ageing temperature suggests that susceptibility to stress corrosion is caused by certain states of precipitate produced at lower temperatures. This view is supported by the further decrease in susceptibility achieved by repeated deterioration of the precipitates and subsequent re-ageing at low temperatures.

Addition of copper to the alloy and two stage ageing at elevated temperatures give a material insensitive enough to stress corrosion for practical use. Additions of about 0.4% silver have been found beneficial and are being further investigated.

1.4 Italy

Work is in hand on the Al/ZnMgCu system at the Instituto Sperimentale dei Metalli Leggeri at Novara. The principal lines of research are:-

- (i) Influence of variations in structure arising from different methods and degrees of working.
- (ii) Search for ageing cycles giving resistance to stress corrosion without appreciable reduction of mechanical properties.
- (iii) Modification of composition for improved stress corrosion resistance.
- (iv) Correlation of structure and properties using the electron microscope.
- (v) Development of a quick valid test for stress corrosion.
- (vi) Further developments.

(i) *Type and degree of plastic working*

Resistance to stress corrosion increases as the number of micro grains increases. The size and shape of the grains are also important. Size and shape are dependent on the type and degree of working and may vary from one point to another in even a simple shape. Too small a grain size, however, increases the corrodibility of the metal because of the greater quantity of intergranular precipitate present and leads to susceptibility to rapid ex-foliation corrosion. Large transverse segregates of intermetallic particles should be avoided.

(ii) *Ageing cycles*

A two stage ageing cycle of 6 hr at 105°C followed by 8 hr at 170°C gives a marked increase in resistance to stress corrosion in the short transverse direction over single ageing in the range 115 to 135°C, accompanied, however, by a fall in 0.2% proof stress of 2 kg/mm² (1½ tons/in²).

(iii) *Modification of composition*

Silver and zirconium have been tried as additions to the traditional alloys or as replacements for chromium and manganese. Zirconium additions allow AlZnMgCu alloys to be quenched slowly, e.g. into oil at 150°C or into a salt bath at 180°C; strength is maintained and internal stresses reduced to a very low level. After preliminary tests on sheet materials, a series of stress corrosion tests was made on transverse specimens cut from extrusions of the basic alloy AlZnMg1½Cu containing Cr, Cr + Ag, Zr, Zr + Ag and Zr + Mn, quenched quickly or slowly, and given single or double ageing treatments.

Three alloys showed high resistance to stress corrosion (axial load in buffered 3% NaCl stressed at 75% of the 0.2% P.S.) without appreciable loss of tensile strength as compared with the 7075-T6 type alloy. These were: (a) the Zr alloy, quenched rapidly or slowly and duplex aged, (b) the Cr + Ag alloy aged at 165 to 175°C, and (c) the Zr + Ag alloy rapidly or slowly quenched and aged at 175°C. Zr + Mn alloy gave poor results. The Zr alloy duplex aged showed no intergranular stress corrosion failure.

(iv) *Structural investigation using the electron microscope*

The stress corrosion properties have been correlated with the mode of precipitation, and the effects of chromium, silver and zirconium interpreted in terms of nucleation, precipitation, the width of precipitate-free zones at the grain boundaries, and stress concentrations set up in the boundaries.

(v) *Tests for stress corrosion*

Two standard tests are used:

- (a) Continuous immersion under axial load, in spring loaded jigs, in 3% sodium chloride solution buffered to pH 5.2 by addition of 8 ml/l N/2 sodium acetate and 20 ml/l N/2 acetic acid, thermostatted at 20° ± 0.5°C.
- (b) Alternate immersion in 3.5% sodium chloride solution under tension or bending load, (fork type), 15 mins in and 45 mins out, at 20°C and constant humidity.

(vi) *Further developments*

Two particular alloys are being further developed:

Al-5.7 Zn-2.3 Mg-1.5 Cu-0.20 Zr-0.06 Ti (Zergal 3)
and Al-5.7 Zn-2.7 Mg-0.5 Cu-0.20 Zr-0.06 Ti (Zergal 4)

Zergal 3 is suitable for all wrought forms, and Zergal 4 should be especially suitable for large forgings. Further alloy development of the AlZnMgCu system is proposed with study by electron microscope of the most promising heat treatment conditions. The role of dislocations in the mechanism of stress corrosion failure will be studied, and in particular the influence of linear defects introduced by quenching and by controlled plastic strain in alloys with different types of hardening precipitate.

1.5 United Kingdom

(i) *General and testing*

Stress corrosion of high strength aluminium alloys is still a major problem. Radical improvements are needed in design philosophy and testing to permit the use of existing alloys with greater safety, and improved alloys are needed to simplify the designer's task and allow the strongest alloys to be used more widely.

Most testing has been carried out at high stresses, and has failed to emphasise that very low stresses can cause cracking, particularly when acting in the transverse and short transverse directions. Although data on threshold stresses have been available from the USA, it has often been impracticable to keep below the threshold and the estimation of safe lives at higher stresses is very difficult because of the need to simulate the environment of the structure and accelerate its effect in a controlled manner. No real progress is being made in estimating the lives of protected parts, but this problem may disappear as the properties of the alloys are improved.

(ii) *Silver additions*

Polmear's suggestion that small additions of silver should improve the stress corrosion resistance of AlZnMg alloys by promoting precipitation in the otherwise precipitate-free zones near the grain boundaries and by refining the precipitate elsewhere, is being investigated at several laboratories. Aluminium Laboratories (Alcan Industries Ltd) have made 3 inch thick plate from 1,000 lb ingots in Al6Zn2.5Mg with different Cu, Mn and Cr contents, with and without 0.3% silver. The silver bearing alloys gave the highest tensile strengths and longest endurances in the Black type stress corrosion tests (atmospheric exposure of transverse specimens at high loads), the alloy containing 1.4 Cu, 0.5 Mn, 0.3 Ag being preferred for its lower quench-sensitivity. Further work has confirmed di Russo's finding that zirconium can replace manganese and chromium, and two compositions containing Cu, Zr and Ag are to be evaluated further. High Duty Alloys Ltd and British Non-Ferrous Metals Research Association, however, have found that silver additions to RR77 (AlZnMg, low Cu no Cr) increase quench sensitivity, decrease strength and give only a marginal improvement in resistance to stress corrosion.

(iii) *Heat treatments*

Some time ago High Duty Alloys Ltd developed a molten salt quenching treatment for the low Cu no Cr alloy, which is now covered by specification DTD 5094; tensile properties are slightly inferior to boiling water quenched material. More recent work has shown that the stress corrosion resistance of the boiling water quenched material can be improved without loss of strength by duplex ageing for 12 hr at 135°C followed by 16 hr at 150°C.

(iv) *Mechanism and structure*

Aluminium Laboratories have studied the relation between susceptibility to stress corrosion and the prevalence of sub-grains in the microstructure. The amount of sub-structure in forgings and plate in commercial AlZnMg alloys was varied by varying the manganese and chromium contents, the hot working procedure, and the quenching rate. In all cases increased sub-structure, or precipitation at sub-boundaries, led to longer stress corrosion lives. More recent work has revealed positive evidence of corrosion and distinct steps of mechanical fracture in the stress corrosion zones. Other studies have shown that a decreased width of precipitate-free zone at the grain boundary gave improved stress corrosion behaviour in high purity AlZnMg alloys, but in commercial alloys zone width seemed less important than other structural features; workers at High Duty Alloys have reached the same conclusions.

Doubts on the benefits of adding silver and of narrowing the width of the precipitate-free zone have led to a modification of earlier views on the formation and significance of precipitate-free zones. Taylor at Cardiff University and Eubury and Nicholson at Cambridge had put forward the view that precipitate nucleated on vacancies formed during solution treatment, and retained by the quench except at grain boundaries which acted as vacancy sinks. More recently Holl's suggestion has been adopted; this is that the vacancy concentration merely controls the rate of growth of clusters of solute atoms (GP zones) formed during quenching and the early stages of ageing, and that the zones must reach a critical size in order to be able to act as nuclei for precipitates.

Both groups now attach much importance to the idea of a metastable phase boundary for GP zones (a GP zone solvus). The temperature of this boundary is determined for each alloy by quenching to and holding at successively lower temperatures in the range 200° to 100°C. So long as the quenching temperature is above the zone solvus, a coarse distribution of precipitates is formed, mainly by nucleation on dislocations. But below the solvus temperature a much finer dispersion of precipitates is obtained, presumably by nucleation on GP zones. Fine homogenous structures can be produced at temperatures above the GP solvus if the alloy is first held at room temperature after conventional cold quenching, or is given a preliminary ageing treatment below the solvus. These preliminary treatments are thought to allow sufficient diffusion for the formation of GP zones large enough to act as nuclei above the solvus.

It seems that these later suggestions about the effects of composition and treatment on the dispersion of precipitate will be more important for the development of alloys resistant to stress corrosion than the earlier work on precipitate-free zones.

2. STEELS

2.1 USA

The loss of load-carrying capability of ferrous structural materials has long been recognised. Of prime concern are the high-strength low-alloy steels, such as SAE 4340, H-11, 300 M, etc, and the high-strength stainless steels of the austenitic, martensitic, and precipitation hardening types. The overall objectives of the various research programmes (see Table II) are to investigate the fundamental factors which control environmentally-induced delayed failures. In general, these studies are divided into two types (a) a study of environmental variables and (b) the influence of metallurgical variables on delayed failure characteristics.

Environmentally-induced failures have been characterised by a decreasing failure time accompanying an increased stress level. Although not completely established, there appears to be a threshold-stress level below which no stress-corrosion-cracking failures occur.

At the present time, environmentally-induced failures of sustained-loaded high-strength steels have been attributed to one or more of the following mechanisms.

1. Stress-corrosion cracking (anodic dissolution).
2. Hydrogen-stress cracking.
3. Stress-sorption cracking (lowering of surface energy at the crack tip due to absorption of a liquid).

Much of the controversy concerning which mechanism is operative in the stress-corrosion cracking of high-strength steels stems from several factors, namely:

1. Depending on the environment, more than one mechanism appears to be operative.
2. The difficulty in distinguishing any differences between fractures caused by hydrogen-stress cracking and those resulting from stress-corrosion cracking.
3. The apparent role played by hydrogen in all the cracking mechanisms.

It seems to be a fairly common thesis among researchers in the US that delayed failures of high-strength steels can be attributed to a single mechanism independent of environment. Much of the research, therefore, is directed toward systematically studying environmental conditions in order to describe a range where transition in embrittling mechanisms occur.

2.2 Canada

Work is in hand in connection with sea-going hydrofoil craft such as the Canadian FHE 400 in which highly stressed foil members are made of 18% nickel maraging steel. It is difficult if not impossible to devise adequate protective schemes for such parts, and susceptibility to stress corrosion is a major problem which can cause the rejection of otherwise acceptable metals. The most promising solution is the development of new high strength alloys not susceptible to stress corrosion and highly resistant to plain corrosion.

Stress corrosion studies of maraging steels are being carried out in the Defence Research Board (R.D. Barer and J. Greenblatt) and in the Physical Metallurgy Division

of the Department of Energy, Mines and Resources (G.J. Bieffer). The work deals with the effects of such factors as surface condition (including cracks, coatings), stress level, cathodic protection potential and heat treatment condition, including weld metal. At the Physical Metallurgy Division, the stress corrosion behaviour of other high strength steels, 17/4PH stainless, 12% nickel maraging and HP9Ni4Co25C, is being evaluated for possible use of the steels in a future generation of Hydrofoils, and is complemented by work on fracture toughness and weldability by R.C.A. Thurston and K. Winterton.

Other work on very strong low alloy steels in the Department of Energy, Mines and Resources is concerned with non-embrittling protective treatments.

2.3 Germany

Fundamental work on caustic and nitrate cracking of iron and carbon steels is in hand at the Max Planck Institut für Eisenforschung at Düsseldorf (H.J. Engell, A. Bäuml and K. Bohnenkamp), at Mannesmann A.G. at Duisburg and at the Badische Anilin- und Sodafabrik at Ludwigshafen, (R. Münster, H. Gräfin and D. Kuron) and mechanisms for failure have been put forward.

Work on stainless steel at Mannesmann (H. Ternes) and at Badische Anilin has contributed to the idea that stress corrosion can occur in homogenous non-supersaturated alloys only if the crack walls become passivated. Experiments at Mannesmann on carbon stabilised austenitic stainless steel in 42% magnesium chloride solution with applied emf showed that stress corrosion cracking could occur even in the absence of oxygen; the crack walls became passivated and hydrogen was discharged, while the flowing root of the crack remained active. Work at Badische Anilin on copper-containing austenitic stainless steels in sulphuric acid was interpreted in terms of local rupture of the protective copper-containing film, but Graf and Springe at the Max Planck Institut at Stuttgart feel that the cause of stress corrosion failure is the formation of cathodic areas, consisting of copper, on the walls of the cracks so that a pronounced electrochemical process can occur within the cracks.

Sensitised austenitic chromium manganese steels have been investigated at Edelstahlwerke Gebr. Böhler at Düsseldorf (A. Bäuml and O. Trampusch). Precipitation of chromium carbide at the grain boundaries and depletion of chromium in solution led to intercrystalline stress corrosion failure. It is not usually practicable to dissolve the carbon by heat treatment.

2.4 Italy

The amount of work on metals other than aluminium alloys is not large. Caustic embrittlement of mild weldable steel is being investigated at the Istituto Ricerche Breda and some studies of stainless steels have been made at the Universities of Milan and Ferrara.

2.5 Norway

No work is in hand at present, but the Central Institute for Industrial Research at Blindern, Oslo, recently completed an examination of the effect of explosive forming on the stress corrosion properties of types 304, 316 and 347 austenitic stainless steels.

2.6 United Kingdom

The stress corrosion properties of three non-stainless steels, a NiCrMoV steel, 5CrMoV, and 18Ni maraging, are being investigated at the Fulmer Research Institute (M.Giles). Specimens are protected by cadmium plate with and without paint, by phosphate treatment and paint, and by sprayed aluminium. In some tests specimens coated with deliberately damaged cadmium plate failed more quickly than unprotected control specimens, although some lasted much longer. Parallel polarisation tests suggest that corrosion-generated hydrogen may have been responsible for the failures. The work is being extended to include Brown tests and thin film electron microscopy (G.Sanderson).

British Iron and Steel Research Association, Sheffield, (M.J.May) are also carrying out Brown tests on several high strength steels. They hope to compare the results with those from standard stress corrosion tests; if the correlation is good, the quicker Brown test could presumably be used instead of the standard test for some purposes.

Stainless steels are being investigated at the Lown-Firth Research Laboratories at Sheffield (J.E.Truman), including polarisation studies. Although results so far obtained were in agreement with those of most previous workers, viz that anodic polarisation in neutral 3% sodium chloride solutions accelerated the failure of tensile type stress corrosion test pieces, and cathodic polarisation at low current densities delayed failure, it was concluded from fractographic evidence that in most conditions the cracking was caused by failure of regions which had become embrittled by corrosion-generated hydrogen. The work was carried out on simple martensitic steels, Fe-13Cr with 0.1, 0.2 and 0.3C which have least resistance to stress corrosion when tempered in the range 350-500°C, but many of the conclusions are considered equally valid for precipitation hardening steels such as FV520S, FV520B and Rex 627 (14Cr5NiCuMoV).

The effect of minor impurity elements on the resistance of FV520S sheet to stress corrosion is being investigated jointly at Bristol Aerojet Ltd, Weston-Super-Mare, (P.F.Langstone) and at British Iron & Steel Research Association, Battersea, London, (K.A.Chandler). The results indicate that small additions of S, P, As, Sn and Al to the high purity base improve resistance and Si and Co are detrimental, but the effects are overshadowed by those of surface preparation; electropolishing, on those compositions to which it gives a smooth, bright surface, imparts a very large improvement in properties.

3. TITANIUM ALLOYS

3.1 USA

Of all materials with a high ratio of strength to weight, titanium alloys are of major interest for a variety of aerospace and hydrospace applications. Titanium alloys were believed at first to be highly resistant to stress corrosion cracking in the environments known to cause failure of stainless steels, low-alloy steels, and aluminium alloys. More recently, stress-corrosion-cracking type failures have been encountered with a number of titanium alloys in such diverse environments as chlorinated solvents, freons, methanol, and nitrogen tetroxide. In addition, it has been found that flaws, notches, fatigue cracks, etc, can be made to propagate in such environments as seawater, distilled water, and dry gaseous hydrogen at sustained stress levels which would not otherwise cause failure. Interest in titanium for use in the supersonic transport (SST) programmes also has rekindled concern for the problem of hot-salt cracking of titanium alloys.

This occurrence of stress-corrosion cracking of titanium alloys under unexpected conditions has stimulated considerable research effort on the part of both government and industry. The research programmes cover a broad spectrum from basic mechanism studies to plain testing and evaluation.

Present information indicates that cracking in most environments, with the possible exception of N_2O_4 , is at least in part electrochemical in nature. The evidence also points to a relationship between susceptible paths for cracking and alloy content, fabrication history, and heat treatment. Both high aluminium and oxygen contents increase susceptibility to cracking. Some evidence also indicates that hydrogen plays a role in the cracking mechanism. However, it does not appear to be one of embrittlement.

Significant progress in improving behaviour of titanium alloys has been made through alloying and heat treatment. Continuing research in this direction is expected to result in the development within the next several years of new alloys having low susceptibility to crack initiation and propagation.

Representative research programmes now in progress, relating to titanium alloy stress-corrosion cracking, are summarised in Table III.

3.2 Canada

A programme of titanium alloy development directed towards improved alloys for Hydrofoil and similar applications is under way in the Physical Metallurgy Division of the Department of Energy, Mines and Resources (H.V.Kinsey) (see Section 2.2).

3.3 Italy

An investigation into the behaviour of titanium and its alloys in non-aqueous liquids such as methanol has been carried out at the University of Milan.

3.4 United Kingdom

Work at Imperial Metal Industries Ltd, Birmingham, on stress corrosion failure of titanium alloys in chlorinated hydrocarbons has been described by J.B.Cotton in his Paper No.7 presented to this Symposium. A small study at IMI using the Brown technique has shown that sodium chloride lowered the K_{IC} of Ti2Cu alloy from 73 to 67 ksi \times inch^{3/2} units, and of Ti6Al4V from 50 to 37. Similar tests have been made at Jessop-Saville Ltd, Sheffield, (H.C.Child and A.L.Dalton) on Ti5Al2 $\frac{1}{2}$ Sn, Ti6Al4V, Ti4Al4Mo2Sn $\frac{1}{2}$ Si (Hylite 50) and Ti6Sn5Zr3Al $\frac{1}{2}$ Si (Hylite 55); the Hylite 50 alloy showed properties superior to the Ti6Al4V alloy despite its higher strength.

G.Sanderson and J.C.Scully at Leeds University have concluded that hydride formation is part of the mechanism by which chloride solutions aid the propagation of existing cracks. Examination of thin foils of the susceptible Ti5Al2 $\frac{1}{2}$ Sn alloy by transmission electron microscopy showed that hydrides were formed in the surface when the alloy was plastically deformed while immersed in 3% sodium chloride solution. This occurred only in susceptible alloys and in environments that cause cracking. Subsequent corrosion and cracking are believed to occur along the interfaces of the hydride matrices, where there is a high density of dislocations. Similar preferential attack has been observed at the long dislocation pile-ups that can be formed in the Ti5Al2 $\frac{1}{2}$ Sn alloy by plastic

straining. The same workers investigated the hot salt cracking of titanium alloys and concluded that dislocation arrays were rendered more reactive by solute atom segregation and were attacked by locally produced chlorine. (See also J.C. Scully in the Discussion on Paper No. 7).

High Duty Alloys Ltd, Slough, (M.J. Rea) have carried out hot salt tests on three titanium alloys used for engine parts. Under sustained load at 350°C, hot salt caused only shallow surface cracking of Ti4Al4Mn alloy, but the ductility determined afterwards at room temperature was much reduced. The Wöhler fatigue properties at 350°C were, however, unaffected by salt. On the remaining alloys (SnZrMoSi types) salt reduced both stress rupture lives and fatigue lives at 450°C. Further tests are in hand.

4. GENERAL COMMENTS FROM THE NATIONAL SURVEYS

4.1 USA

(a) *Introduction*

Corrosion and corrosion protection are matters of national concern. Each year the United States government spends tens of millions of dollars for corrosion and related studies.

By far, the area receiving major effort is that concerned with the premature cracking of structural materials due to the action of environments, generally referred to as "Corrosion Cracking" (this term includes both stress-corrosion cracking and associated hydrogen embrittlement or hydrogen-stress cracking). This is not surprising in view of the catastrophic nature of the corrosion-cracking failure process, its interest to the scientific community, and the critical concern of military and industrial establishments.

(b) *Research philosophy*

It is fairly well recognised by our scientific and engineering community that one of our most serious technical problems is the tendency toward stress-corrosion cracking and related phenomena in high strength-to-weight ratio materials. The problem is particularly critical with alloys used in advanced aeronautical vehicles and undersea structures and vessels. Many of our problems exist today, while others are known to exist in systems now in various stages of development. Basically, our problem with stress-corrosion cracking arises from having to use materials for reasons other than corrosion resistance, and from difficulties in following through from research and development to application.

The desire on the part of the Air Force, Army, and Navy research agencies to develop an effective communications link between the theoretical researcher and the engineer has resulted over the past few years in a significant change in the US research philosophy governing corrosion research goals. Most corrosion research used to be done after the fact. That is, the programmes were designed to find a solution for an existing specific problem, with only secondary interest in mechanism and interaction of metallurgical and environmental factors or why the protection scheme was effective. In addition, much of the research suffered from lack of co-ordination with an overall goal and often the useful information developed was not disseminated to those who could use it to best advantage.

Today, however, the philosophy is one of coupling, that is, creating an atmosphere in which the basic researcher, the applied scientist, and the engineer can be brought together so as to develop greater familiarity with each other's problems. We have the distinct feeling that the theoretical and academic researchers would be more selective in their area of study and provide more effective guidance to students if they had a greater appreciation of applied problems and their importance. By the same token, much more of their research might be utilised if the engineer could visualise how research on seemingly isolated and idealised problems related to the complexities of in-service situations.

(c) Corrosion coupling programme

Perhaps the largest single effort in the USA directed almost entirely to developing a solution to stress-corrosion cracking and related phenomena is the multi-million dollar coupling programme sponsored by the Advanced Research Project Agency (ARPA). The theme of the programme is Environmental Cracking as it applies to all metallic systems. However, primary effort is being directed toward three different structural systems as represented by titanium alloys, aluminium alloys, and low-alloy high-strength steels.

The programme is under the leadership of the Naval Research Laboratory with portions of the integrated effort being conducted by industry (Boeing Company) and universities (Lehigh, Carnegie Institute of Technology, and Georgia Institute of Technology). A summary of the areas of research and the programme directors for each area is presented in Table IV.

The programme basically considers that there is a spectrum between 100% mechanical factors and 100% chemical-electrochemical factors and that the controlling factors for any given alloy system will be somewhere in between. It is further assumed that environmental conditions will change the proportion of mechanical and chemical factors for both the initiation and propagation of cracks in a manner depending on the alloy system. Another consideration is that flaws already present in a structure will propagate under loads and that a corrosion process such as pitting is not necessarily a prerequisite to cracking. Some of the important component processes presently under investigation are: anodic and cathodic processes, dislocation-surface interactions, dislocation-crack interactions, film formation, environmental bulk fracture phenomena, and metallurgical and process variables. On the more practical side, one phase of the research concerns the development and evaluation of test techniques for the evaluation of the susceptibility of an alloy to stress-corrosion cracking. Care is being taken to ensure that such tests will be sensitive to the wide range of environmental conditions in critical service applications, both by industry and the military.

A smaller effort, which reflects the coupling theory, is being sponsored by the Air Force Materials Laboratory (AFML) at The Ohio State University. This study, like the ARPA programme, is concerned with fundamental and applied aspects of environmental cracking. In the main, the research is concerned with those materials and environmental conditions encountered by the Air Force. The programme is so designed that students doing basic research spend time at the AFML learning first hand current and future Air Force problems and needs. The programme is under the direction of Dr M.G. Fontana, Chairman, Department of Metallurgy, The Ohio State University.

Details of projects have already been listed under the headings Aluminium Alloys, Steels, and Titanium Alloys.

Neither of these integrated programmes has yet been in effect for a sufficient time to provide a significant impact on present theory. It is expected, however, that such programmes will provide the basis for an understanding of environmental fracture mechanisms for structural materials, and will point out those directions most fruitful to the development of alloys having a low susceptibility to stress-corrosion cracking at high-stress levels.

(d) *Other metals*

The stress-corrosion-cracking characteristics of austenitic stainless steels is still of considerable interest in the US. For the most part, these studies are centred around compositional variations, both alloying and impurity elements, which influence susceptibility to cracking.

Some research is also in progress on both magnesium and beryllium-base alloys. This effort, however, is minor when compared to that on other structural materials.

4.2 Germany

Besides the work on specific structural metals, a fundamental investigation into the mechanisms of stress corrosion failure is in hand at the Max Planck Institute at Stuttgart. An outline of the present conclusions from this work has already been given by Professor L. Graf in the discussion on Paper No. 1, General Theory.

5. DISCUSSION ON NATIONAL SURVEYS

Professor Nutting was surprised at the apparent lack of interest in the stress corrosion of copper base alloys; such work was useful for gaining basic understanding. Mr Boyd said there were several projects in the USA at universities and in the laboratories of the copper producing companies, concerned, for instance, with the tolerable concentration of ammonia and with inhibitors. These projects were not, however, co-ordinated into the programmes on structural metals. Professor Graf drew attention to his work on fundamentals which included work on copper base materials.

Mr Evans recalled the influence of the pH of the environment on the SCC of aluminium alloys. Might it not be an advantage to add to a paint primer not only an inhibiting chromate pigment but also a buffering agent? Professor Graf quoted Matson's finding, that the SCC of brass was very dependent on pH. The pH determined whether the passive film on the crack walls was cupric or cuprous oxide. Below pH 2 no film formed and hence no SCC occurred because the cathode wall was not enobled.

Squadron Leader Vernon spoke up again for the user. Greater care was needed during design and manufacture. Detail design drawings should be overseen by qualified metallurgists who would understand the problems likely to arise. The manufacturing sequence should be such that compressive stresses were present in, or introduced into, the surface, and tensile stresses avoided. Better quality control of final machining was needed. Machining was often subcontracted at production piece rates. Fast and heavy

cuts were sometimes taken, giving local heating and leaving tool marks often on surfaces hidden from view; many of the failures in RAF service had started at such surfaces. Although advances in surface protection offered the least promise for improvements in resistance to SCC, improvement in protective schemes would be welcome. All external surfaces of RAF aircraft would in future be protected by chromate pigmented epoxy polyamide primer followed by a polyurethane top coat; the protection of internal surfaces at present often left unpainted, needed further thought.

The maintenance officers problem was the complete unpredictability of where and when a stress corrosion crack might start, and the knowledge that the subsequent rate of crack propagation might be high tended to reduce confidence in aircraft structures. Design authorities had at no time predicted the occurrence of stress corrosion or forecast a point of initiation. The maintenance officer's task was to decide what and where to examine, when to start examining and how frequently to repeat the examination. Inspection was often hindered by limited access and complex non-destructive techniques were needed. It would be of the greatest value to have a non-destructive test which would reveal high residual stresses in installed components.

In common with other users of aircraft, the RAF had at one time a serious problem with fatigue. Fatigue was now reasonably estimated and controlled, but SCC remained an outstanding problem. Were it not for the development of non-destructive techniques for the detection of cracks, many flying hours would have been lost and operational aircraft grounded.

Mr H.R. Ashley said there was no doubt that the effects of stress corrosion in aircraft structures had been costly in time and money. Some self criticism was needed. He thought two points in particular had arisen during the Symposium.

The first was the coming together of what used to be thought of as separate subjects, viz fatigue, crack propagation, fracture toughness, stress corrosion resistance, internal stress and residual strength. The engineer must include consideration of all these properties in his design. It was now more easy to see that the specialists in all these fields were working to one end. If the Symposium had helped to bring about a fusion of skills in all these fields, then it would have been well worth while.

Secondly, international standards were needed for tests for resistance to SCC. We had heard reference to the Brown test, the Boeing test, the Black and the Vickers tests and the Schmittkanten method. Many of the results from these tests could not be directly compared. A modified Boeing test might be considered, using constant load instead of constant strain. The Brown test had the merit of speed, and of including a notch effect from the outset. All aspects of these tests needed careful consideration, and an international lead would be welcome to all.

TABLE I
Typical Research Studies Relating to Stress-Corrosion Cracking of Aluminium Alloys

Laboratory	Principal Investigator	Scope of Programme
Rocketdyne	A. J. Jacobs	Mechanism of stress-corrosion cracking in aluminium alloys
Battelle-Columbus Laboratories	W. K. Boyd and F. H. Haynie	Role of H_2 in stress-corrosion cracking of aluminium alloys and mechanical aspects of stress-corrosion cracking
Alcoa Research Laboratories	D. O. Sprohls and W. W. Binger	Mechanisms of stress-corrosion cracking, methods of protection
Aeronautical Materials Laboratory Naval Air Engineering Centre	S. J. Ketcham and J. J. De Luccia	Stress-corrosion cracking in 7075 aluminium alloys
NASA-Marshall Space Flight Centre	W. R. Lucas	Stress-corrosion cracking susceptibility of high-strength aluminium alloys
Kaiser Aluminium and Chemical Corporation	T. Summerson	Development of a rapid stress-corrosion cracking test for aluminium alloys
National Bureau of Standards	P. M. Reinhardt	Directional effects in the stress-corrosion cracking of aluminium alloys
Tyco Laboratories	-	General mechanism studies and development of techniques for detection of stress-corrosion cracking
IIT Research Institute	F. A. Crossley	Corrosion of aluminium alloys
Reynolds Metals	H. L. Craig, Jr	Stress-corrosion mechanism and rapid tests
Douglas Aircraft - Long Beach	C. H. Avery	Applied research
Frankford Arsenal	H. R. Pretchard	Mechanism studies
Wyman Gordon Company	-	Manufacturing process for improving stress-corrosion cracking resistance of aluminium forgings

In-house research studies on stress-corrosion cracking of aluminium alloys and means of preventing stress-corrosion cracking are being conducted by a number of aircraft companies and Government laboratories.

TABLE II
Typical Research Relating to Stress-Corrosion Cracking of Ferrous-Base Alloys

Laboratory	Principal Investigator	Scope of Programme
US Steel Applied Research Laboratories	E. H. Phelps	Mechanism, metallurgical, and environmental aspects of stress-corrosion cracking
International Nickel Company Sterling Forest, N.Y.	D. Van Rooyen	Mechanisms
University of Wisconsin	R. A. Dood	Carbon and nitrogen effects in stainless steels
Carnegie Institute of Technology	H. W. Paxton	Effect of high nitrogen on stress-corrosion cracking
Ohio State University	M. G. Fontana and R. W. Staehle	Stress-corrosion cracking mechanisms of Fe-Ni-Cr alloys
Cornell University	H. H. Johnson	Environmental factors in crack growth
Standard Research Institute	D. L. Douglass	Mechanisms
Battelle-Columbus Laboratories	W. K. Boyd and A. R. Elisea	Mechanisms and hydrogen-stress cracking
Naval Applied Science Laboratory	W. L. Miller	Electrochemical factors in stress-corrosion cracking
Armco Steel Company Baltimore Laboratories	E. E. Denhard	Stress-corrosion cracking of high-strength stainless steels
TRW Equipment Laboratories	E. A. Steigerwald	Stress-corrosion cracking mechanisms in martensitic high-strength steels
Northrop Corporation	G. V. Seamore	Accelerated stress-corrosion cracking tests for ferrous and nickel-base alloys
Naval Research Laboratories	B. F. Brown	Fracture mechanics in stress-corrosion cracking
Douglas Aircraft	N. A. Tiner	Role of hydrogen in stress-corrosion cracking of high-strength steel and susceptibility of 9Ni-40Co high-strength steels
Du Pont Research Laboratory	N. A. Nielson	Microfractography of stress-corrosion cracking
Massachusetts Institute of Technology	H. H. Uhlig	Mechanism of stress-corrosion cracking in controlled purity materials

TABLE III
Typical Research on the Stress-Corrosion Cracking of Titanium Alloys

<i>Laboratory</i>	<i>Principal Investigator</i>	<i>Scope of Programme</i>
Naval Research Laboratory	B. P. Brown and C. D. Beacham	Fracture mechanics concepts in stress-corrosion cracking
NASA - George C. Marshall Space Flight Centre	W. R. Lucas	Environmental stress-corrosion cracking of titanium alloys
NASA - Langley Research Centre	George Hummel	Hot salt and other environmental studies of stress-corrosion cracking of titanium alloys
Ohio State University	F. H. Beck	Basic studies of environmental factors relating to stress- corrosion cracking of titanium alloys
Mellon Institute	E. G. Hanny	Fundamental mechanism studies
Battelle-Columbus Laboratory	W. K. Boyd and R. I. Jaffee	Interaction of chemical and metallurgical factors influencing stress-corrosion cracking of titanium alloys
NASA - Manned Space Flight Centre	R. E. Johnson	Environmental studies
Bureau of Standards	J. R. Ambrose	Fundamental mechanism studies
Du Pont Savannah River Laboratories	S. P. Rideout	Stress-corrosion cracking in hot salt
Boeing Scientific Research Laboratory	T. R. Beck	Electrochemistry of titanium stress-corrosion cracking
North American Aviation - Downey	Robert O' Brien	Environmental cracking studies
Reactive Metals	H. L. Bomberger	Metallurgical and chemical aspects of stress-corrosion cracking, effects of processing variables
Titanium Metals Corporation	Robert Kane	Metallurgical and chemical aspects of stress-corrosion cracking, effects of processing variables

TABLE III (Continued)

<i>Laboratory</i>	<i>Principal Investigator</i>	<i>Scope of Programme</i>
Bell Aerosystems	Henry Heubusch	N ₂ O ₄ studies
Lockheed Aircraft Company - Sunnyvale	Ken Weber and Joe Reyniewicz	Applied aspects of stress-corrosion cracking
Martin - Denver	S. Goel and W. D. Rummel	Various
Douglas Aircraft - New Port Beach	N. A. Tiner and N. G. Tupper	Mechanism studies
Douglas Aircraft - Santa Monica	Guy Bennett	Applied studies
Air Force Materials Laboratory	Howard Zoeller and Ben Cohen	Applied studies
General Dynamics/Convair - San Diego	Abe Hurlick	Applied studies

In addition to the above, research on various aspects of titanium stress-corrosion cracking is being conducted at most aircraft company laboratories, Government laboratories, and universities.

TABLE IV

ARPA Corrosion Coupling Programme

NAVAL RESEARCH LABORATORY

B.B. Brown, Director
R.A. Meussner, Deputy Director
E.P. Dahlberg, Assistant Director

areas: electrochemistry, surface chemistry, oxide films, stress corrosion of high-strength steels, electron fractography, low-cycle fatigue, fracture mechanics concepts, strain hardening effects

BOEING COMPANY

R.V. Carter, Principal
D.E. Piper, Alternate

areas: generation and computerisation of mechanical test data, selection and characterisation of steels, Al, and Ti, advanced testing concepts, basic studies

CARNEGIE INSTITUTE OF TECHNOLOGY

H.W. Paxton, Programme Director

areas: surface physics, cracking of austenitic steels, plastic deformation, electrochemistry

LEHIGH UNIVERSITY

P.C. Paris, Project Director
A.C. Zettlemoyer, Director, Surface Chemistry Centre

areas: fracture mechanics, surface chemistry

GEORGIA INSTITUTE OF TECHNOLOGY

R. F. Hochman

areas: LEED studies, electrochemistry, structure